

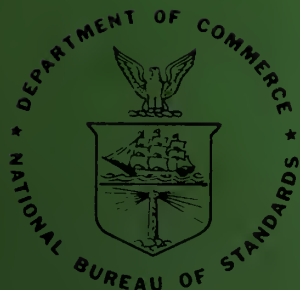
NBS

TECHNICAL NOTE

277

Analytical Mass Spectrometry Section:

**Instrumentation and Procedures
for Isotopic Analysis**



**U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards**

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TECHNICAL NOTE 277

ISSUED July 25, 1966

Analytical Mass
Spectrometry Section:
Instrumentation and Procedures
for Isotopic Analysis

Edited by William R. Shields

Analytical Mass Spectrometry Section
Analytical Chemistry Division
Institute for Materials Research

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

FOREWORD

The Analytical Chemistry Division was established as a separate division at the National Bureau of Standards on September 1, 1963, and became part of the Institute for Materials Research in the February 1, 1964 reorganization. It consists at present of nine sections and about 100 technical personnel encompassing some 45 different analytical competences from activation analysis and atomic absorption to vacuum fusion and X-ray spectroscopy. These competences, and in turn the sections which they comprise, are charged with research at the forefront of analysis as well as awareness of the practical sample, be it standard reference material or service analysis. In addition it is their responsibility to inform others of their efforts.

Formal publication in scientific periodicals is highly important. In addition, however, it has been our experience that informal, annual summaries of progress describing efforts of the past year can be very valuable in disseminating information. At the National Bureau of Standards such publications fit logically into the category of a Technical Note. In 1966 we plan to issue these summaries for all of our sections.

W. Wayne Meinke, Chief
Analytical Chemistry Division

PREFACE

The basic function of the Analytical Mass Spectrometry Section is to establish high accuracy absolute isotopic ratio standards. To this end the section is concerned with developing instrumentation and devising analytical techniques which will improve the precision of isotope ratio measurements; and with performing the actual measurements. In addition, the section is concerned with monitoring both natural and man-made variations in the isotopic composition of elements. Delimiting natural variations is vital to establishing the constancy of atomic weights and is also of general interest to earth scientists.

This report summarizes the major works performed by the personnel of this section over the past eight years. It is primarily designed as a "cookbook" of analytical techniques for isotopic ratio measurements of various elements, and as a guide to the pitfalls encountered in attempts at very precise or accurate isotopic ratio measurements. The report fits the formal description of a Technical Note in the sense that the material is "transient". The instrumentation is continuously being improved and modifications in analytical procedures, which might improve precision, are always being sought.

E. J. Catanzaro and E. L. Garner wrote the descriptions of the analytical procedures; W. A. Bowman, III drafted the schematics; and H. H. Ku, of the Statistical Engineering Section, wrote the appendix. Mrs. Joy Shoemaker typed the report.

In order to describe the instrumentation adequately, it has sometimes been necessary to identify certain commercial equipment. Such identification does in no way imply recommendation or endorsement by the NBS nor does it imply that said equipment is necessarily the best available for the purpose.

William R. Shields, Chief
Analytical Mass Spectrometry Section

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ANALYTICAL MASS SPECTROMETRY SECTION:
INSTRUMENTATION AND PROCEDURES FOR ISOTOPIC ANALYSIS

Edited by William R. Shields

ABSTRACT

This report describes the general instrumentation of the Analytical Mass Spectrometry Section and the specific analytical techniques which have been devised for the measurement of isotopic ratios of Ag, Br, Cl, Cr, Cs, Cu, Mg, Pu, and U. Interim procedures for B, Li, Rb, and Sr are also given.

In the appendix some general statistical principles used in the design and analysis are briefly discussed; an example is given in detail illustrating the various steps involved leading from original data to the reported uncertainties for the isotopic ratio of bromine.

Key words: Mass spectrometry, instrumentation, procedures, isotopic analysis.

A. INTRODUCTION

The present analytical instrumentation of this section consists of five mass spectrometers; three with 12-inch radius of curvature and two with 6-inch radius of curvature. All components are interchangeable within each size group and electronic components and vacuum systems are interchangeable among all of the instruments.

The instruments are nominally solid-source but are readily convertible to gas-source by the attachment of a gas inlet system and an electron bombardment source.

The basic instrument (figure 1) is a composite of commercial and NBS-built components, the latter usually being either slight modifications of commercially designed components or copies of components designed in other laboratories. The instruments are unique only in the combination of the various components. Figures 2 through 7 are the NBS-built electronic circuits.

The more important characteristics of these instruments concern the source, collector, and recording systems. The ion source (figure 8) is a linear thin lens source with each succeeding lens being approximately twice as far from the ionizing filament as the previous lens. The source is made as wide open as possible (no baffles or skirts) to maintain as high a vacuum as possible in the region of the ionizing filament, and a liquid nitrogen cold finger has been installed in the source region to increase the pumping speed for condensables. At the same time, the source housing is made as large as practical to minimize the penetration of the ground potential of the walls into the ion region.

The collector used in the NBS instruments (figure 9) was designed to improve the collection efficiency of the conventional 50% transmission grid collector. The major change from the conventional collector is the six suppression grids made of fine wire that are located between the transmission

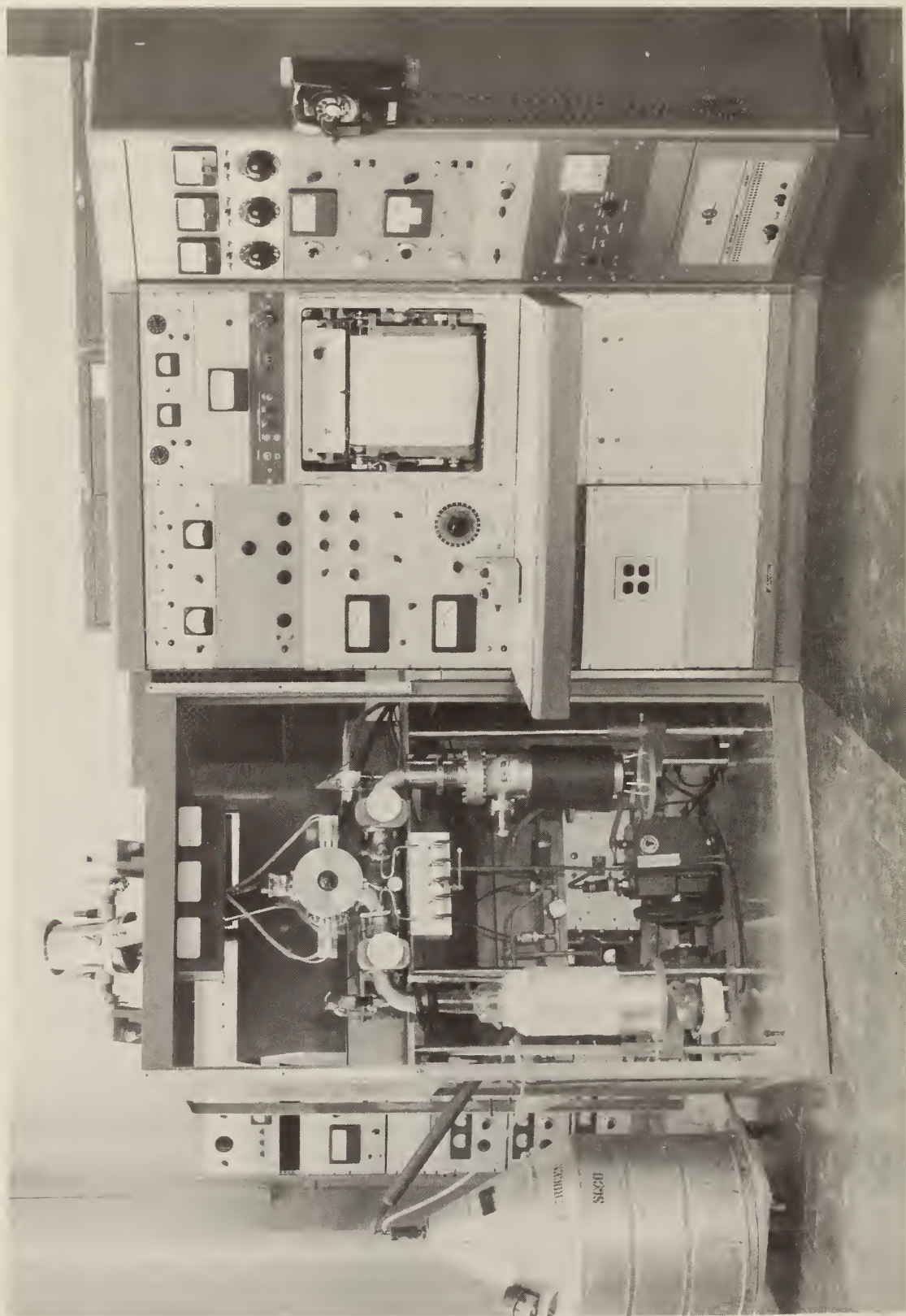


Figure 1. 12" Solid Source Mass Spectrometer

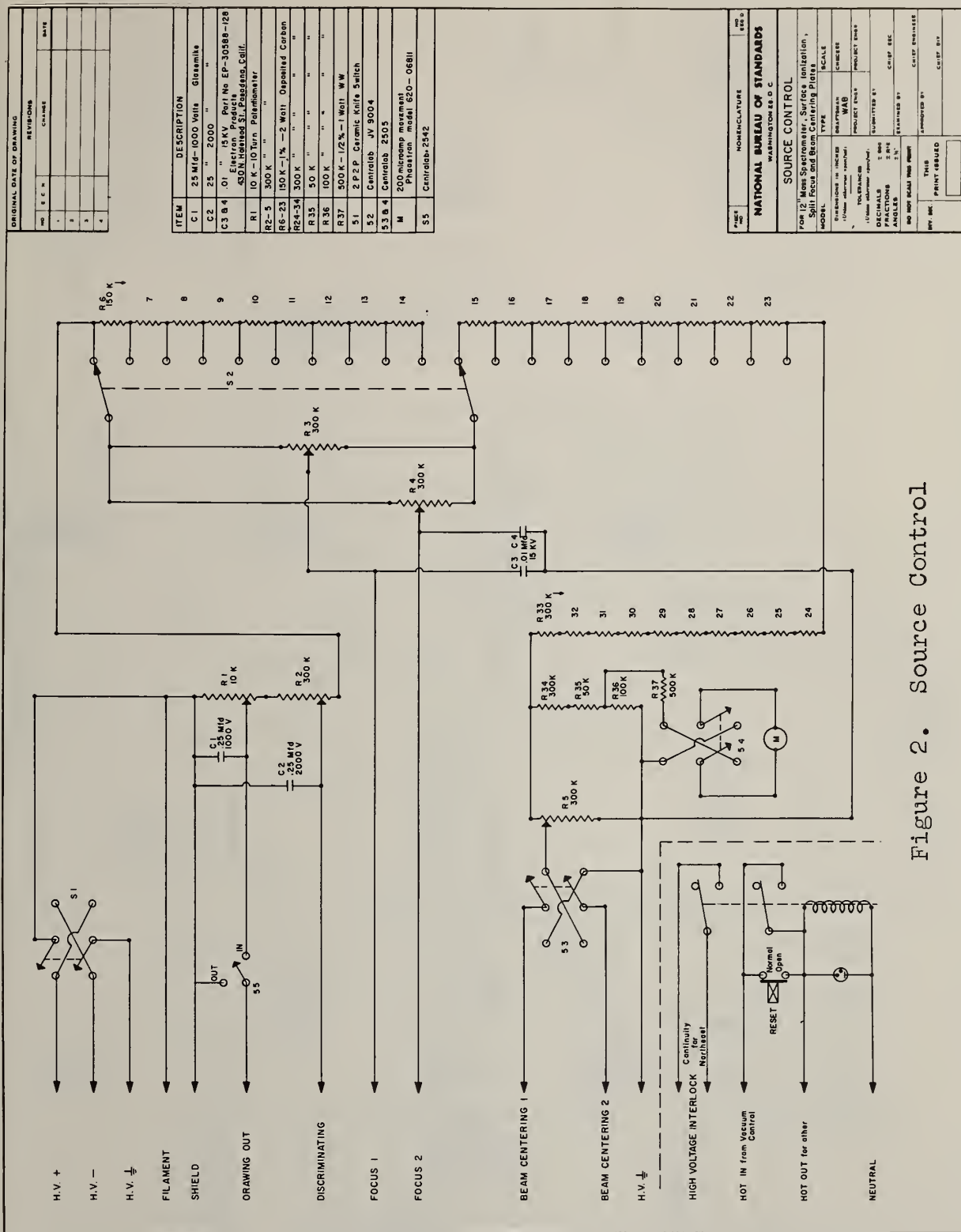
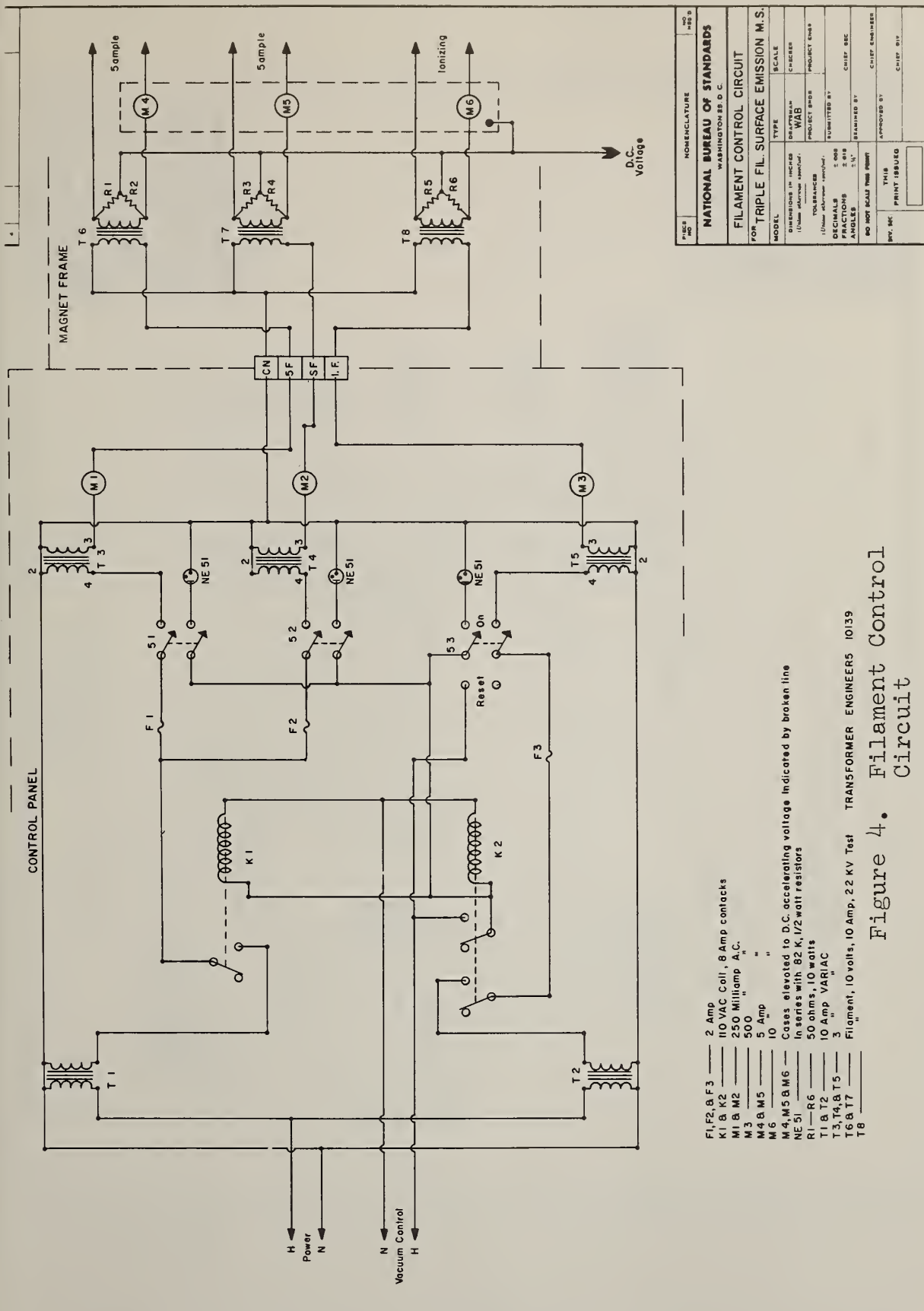
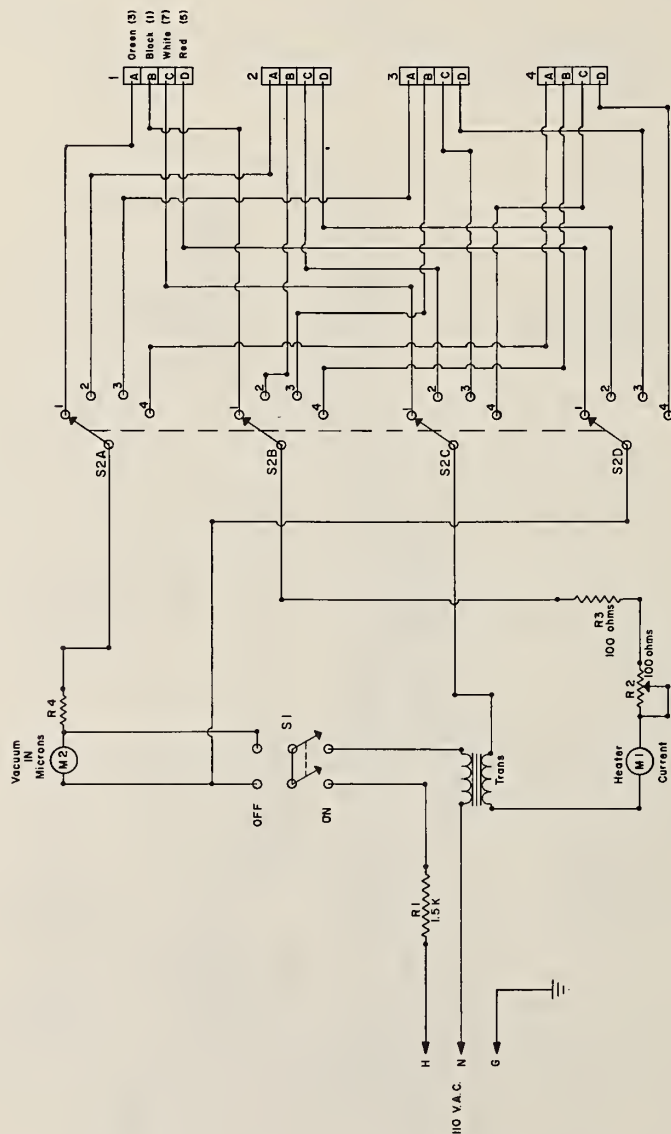


Figure 2. Source Control



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M1 — 50 Milliamp A.C. meter
 M2 — 250 Microamp O.C. meter
 R1 — 1500 ohms 10 watts
 R2 — 100 ohms 10 watts
 R3 — 100 ohms 10 watts
 R4 — meter calibrate
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Figure 5. Thermocouple Vacuum Gauge

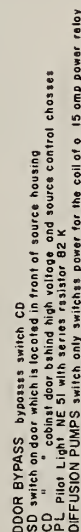
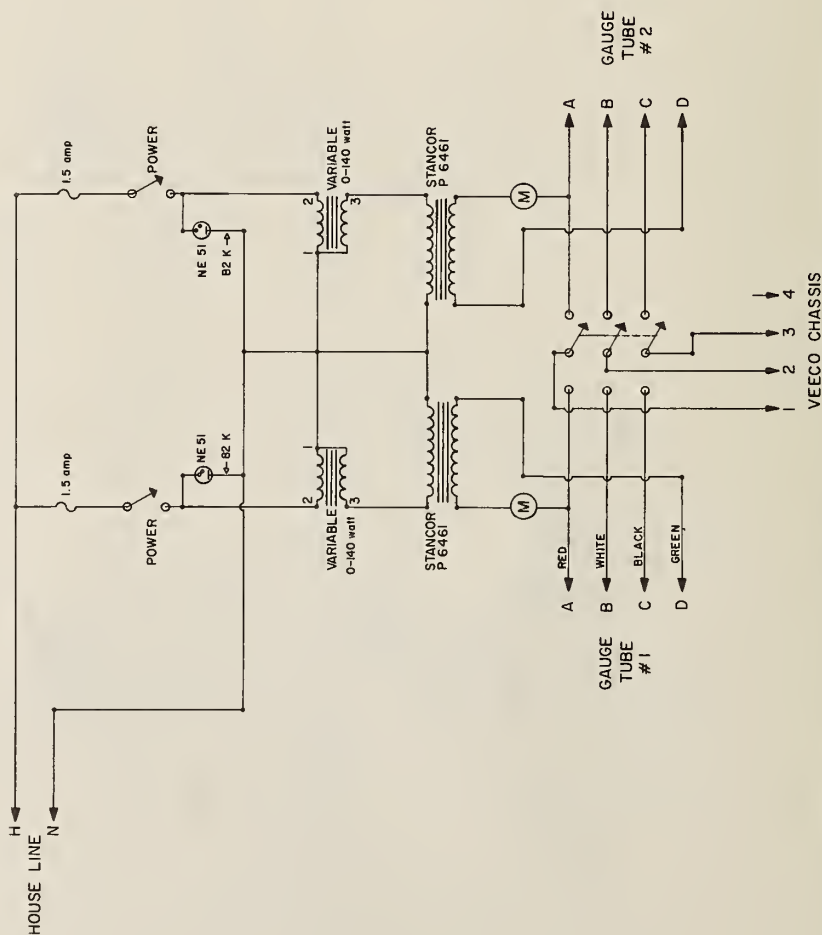
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Figure 6. Vacuum Control Circuit

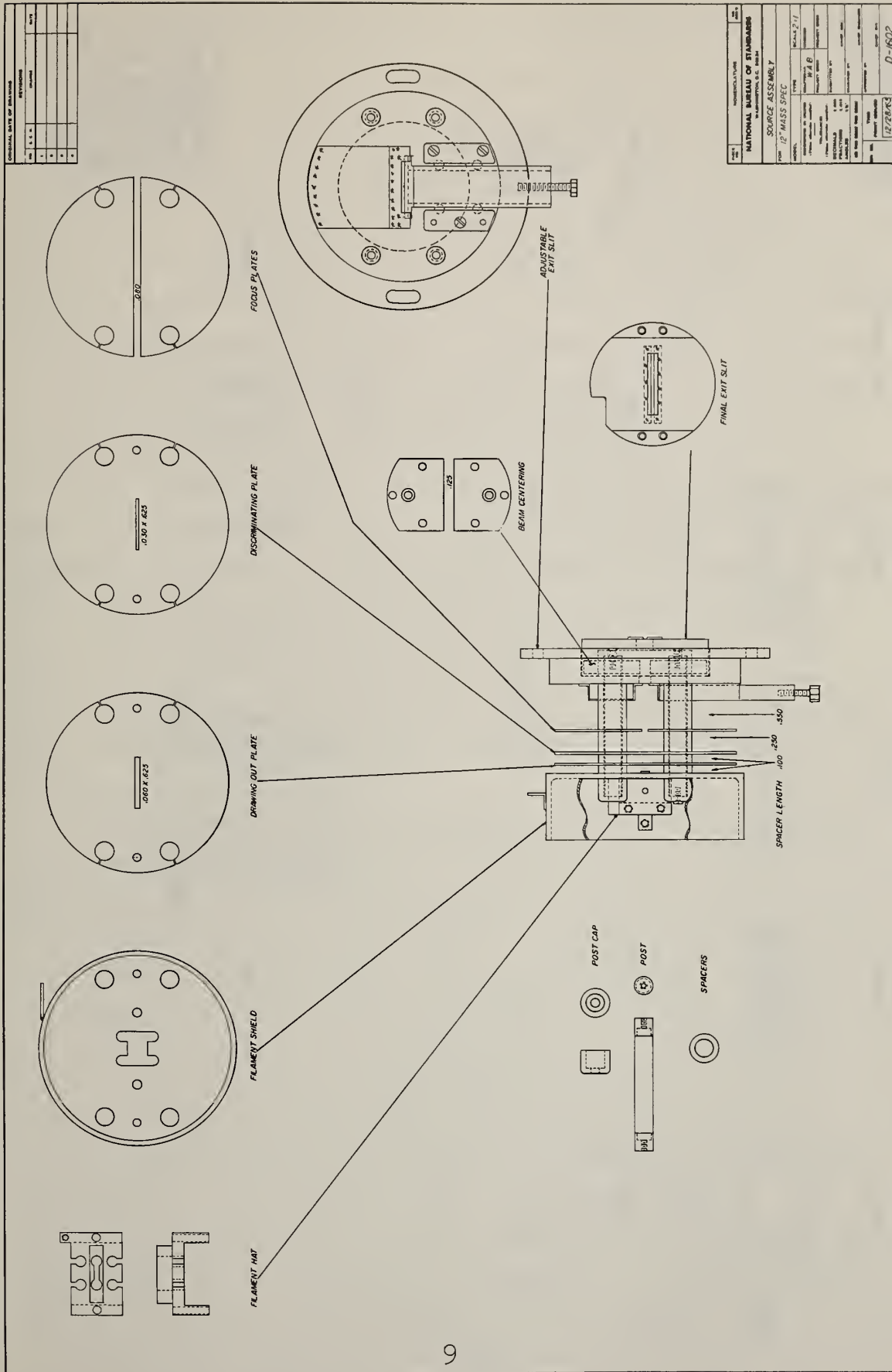
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Figure 7. Ionization Gauge Degas Control

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grid and the defining slit of the collector. (A plate with grid wires on both top and bottom acts as two grids.)

The suppression grids give the operator the ability to control the secondary charged particles, both positive and negative, and when the appropriate potentials are applied to the grids it is possible to obtain the same measured isotopic ratio, for a given sample, with both the expanded scale $\times 10$ and the ratio modes of measuring. The ability to control the grid response made it possible to prove conclusively that variations in grid response are reflected in the measurement of ratios measured solely with the Faraday cage collector. The magnitude of this random bias component is only a few tenths of a percent but it varies with isotopic concentration. One of the properties of the suppression grids is the ability to maintain a fairly constant grid response independent of the ion species and age or cleanliness of the collector.

A small bar magnet strapped to the outside of the collector housing, axially aligned with the ion beam and at 45° to the defining slit, helps control secondary electrons that are released before the entrance to the collector assembly.

The measuring circuit consists of two vibrating reed electrometers (Applied Physics Corps. MS-31), a master and a slave, and an expanded-scale recorder. The slave unit monitors the total signal intensity while the master unit measures the ions striking the Faraday collector. The input resistors for the master and slave reeds are 10^{11} and 10^{10} ohms, respectively. The expanded-scale circuit (figure 10) utilizes the 10 mV and 100 mV signals of the master VRE. A reference source coupled with the push-pull decade provides the other half of the input to the chopper stabilized difference amplifier contained in the recorder. The recorder is a Leeds and Northrup $X_1 - X_2$ model G Speedomax with 1 second response time. The slidewire is shunted to a resistance of 110 ohms for 110 division chart over $9 \frac{7}{8}$ travel. The function of the expanded scale circuit

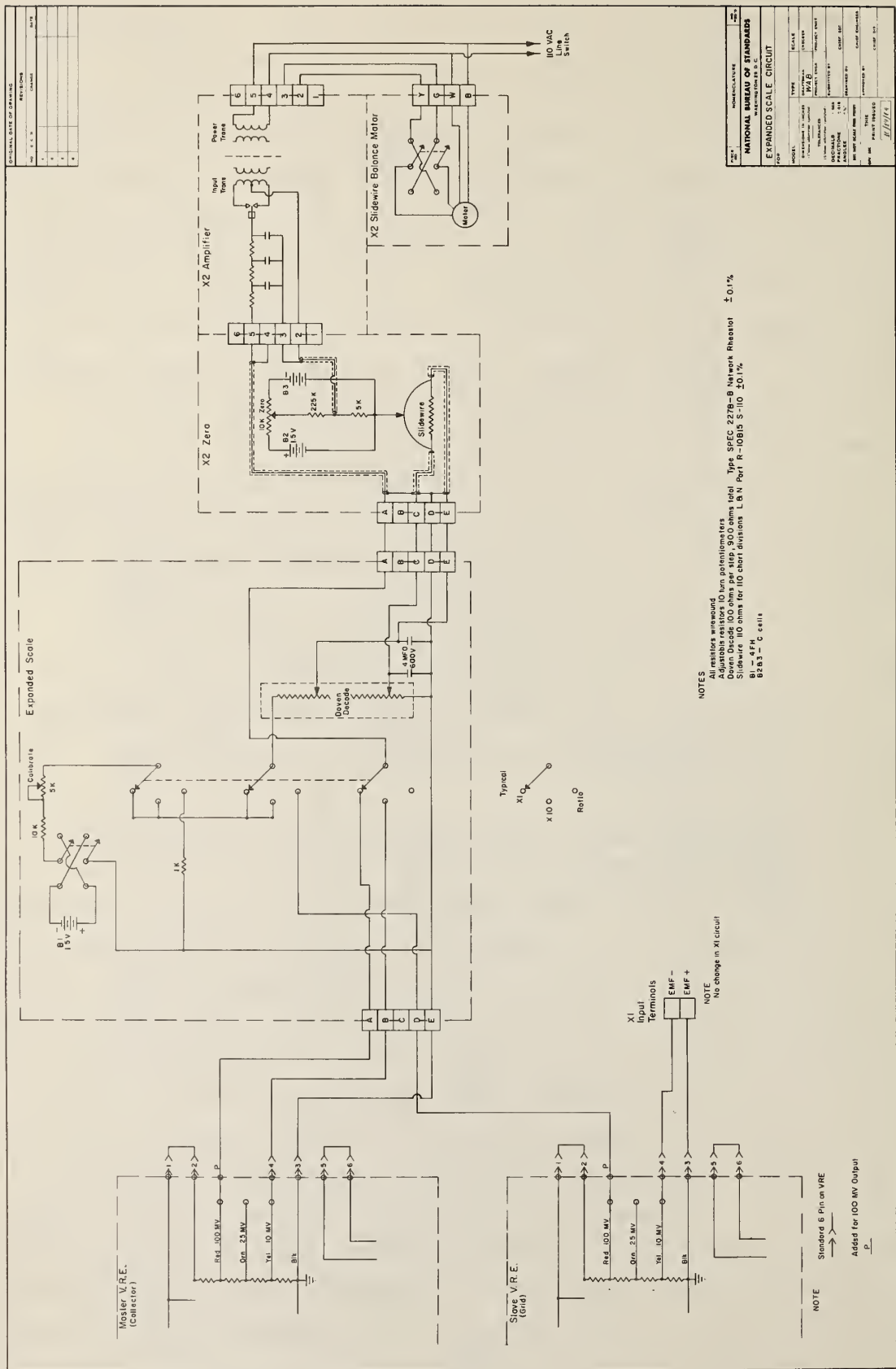


Figure 10. Expanded Scale Circuit

is to increase the normal 100 division full-scale output of the null-balance bridge to 1000 divisions in precise proportional steps of 10% of that output. This improves the operators ability to intercompare the potentials generated by the various isotopes and reduces the bias errors inherent in the servo balance system (dead zone and non-linearity) by an order of magnitude. It should be noted that this circuit maintains its precise proportionality independent of the reference potential.

The function switch in the expanded scale circuit (figure 10) allows the operator to use the recorder and the two amplifiers in three different ways:

- X1) The function switch selects the 10 mV output of the VRE and full-scale output of the amplifier equals 100 chart divisions on the recorder.
- X10) The function switch selects the 100 mV output of the VRE and full-scale output of the amplifier equals 10 full chart widths. By selecting the proper position for the slidewire, with the slidewire position switch, the operator can make the recorder balance and the first digit of the potential being measured is read on the slidewire position switch. The end result is that any systematic error contributed by the recorder has been reduced by one order of magnitude.
- Ratio) With the function switch in this position, the 100 mV output of the grid VRE is used as the reference potential of the recorder and the 100 mV output of the Faraday VRE is fed to the recorder. This function will measure a ratio of ratios independent of intensity, if the collector efficiencies are independent of intensity.

Solid source isotopic measurements generally show a bias when referenced to the absolute ratio of the element in question. A number of the individual bias components whose

sum constitutes the total bias have been identified. The order in which the identified bias components are discussed is essentially the actual order of their identification. This order was chosen because in many cases it was not possible to detect and/or identify certain terms until modifications were made on the instrumentation.

The simplest way to demonstrate the methods used to identify many of the error components is through the use of well documented experimental data:

Ref. 1: Report Number 8, A.E.C. Advisory Committee for Standard Reference Materials and Methods of Measurement, May 1960.

Ref. 2: Proceedings ASTM E-14 Conference, May 1965, p. 157.

Ref. 3: Proceedings IAEA Symposium on Nuclear Materials Management, September 1965.

Figure 11 is a pictogram that clearly displays several sources of experimental bias. In fact it supplies an example of both types of bias (systematic and random) as evaluated through the use of NBS isotopic standards. The data were supplied by laboratories in both Europe and the United States and shows a first partitioning of the variance components that constitute the uncertainty of a large number of isotopic analyses done by surface or thermal ionization. In general, the error components identified are not restricted to a single element, but rather are found to exist for all elements at various levels. All of the data shown had previously been corrected for all known sources of bias by the workers at the various laboratories (ion multiplier discrimination, etc.) and had a calculated analytical precision of better than a 0.25%. A very cursory examination of figure 11 reveals three obvious bias factors: one due to the difference in the mode of ionization, evidenced by the average 1.1% bias of the single filament - dc amplifier results; and another due to the mode of collecting and measuring the ions, evidenced by the

EXPERIMENTAL $^{235}\text{U}/^{238}\text{U}$ VS NBS BEST ESTIMATE 1958

AVERAGE SINGLE FILAMENT
EQUIPPED WITH I/Q MULTIPLIER
AVERAGE MULTIPLE FILAMENT

RATIO OF RATIOS

ASSAY LEVEL 0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100

AVERAGE SINGLE FILAMENT

EQUIPPED WITH D.C. AMPLIFIER
AVERAGE MULTIPLE FILAMENT

Figure 11.

average 0.55% bias superimposed on the results of both modes of ionization when a multiplier is used. Finally, superimposed on both of these systematic errors, is a random error or average limit of error of bias of approximately 0.5%. The random error is made up of several components, the most important of which is due to the strip chart recorder. Manufacturers of strip chart recorders have for years supplied the information that new recorders have possible errors of 0.1% (full scale) in dead zone and 0.25% (full scale) in linearity. Still, the recognition that these parameters are the limiting factor (0.5% LE of bias) on the precision of most isotopic analyses is, unfortunately, not widespread. The expanded scale recorder was developed to circumvent this limitation. The modified recorder, rather than a variety of available digital output systems, was chosen because it is felt that visual interpretation and integration is necessary to do the most precise work.

B. ANALYTICAL PROCEDURES

1. Introduction

After the instrumental bias components have either been removed or have been controlled and corrected for, most solid source mass spectrometric isotopic analysis still show a bias. For a given instrumental setup and element this bias is more or less constant. The magnitude and range of variation of this bias component can be controlled. The fact that elements isotopically fractionate during thermal ionization is well known. The fact that this fractionation factor is variable and is a function of the sample size and sample composition interacting with the filament material and filament temperature is not so well known. This variable fractionation factor (bias) has been observed in all elements analyzed at this laboratory. For many of the elements analyzed in this laboratory slight changes in the chemistry of the sample, or the manner in which the sample is mounted on the filaments, will have dramatic effects on the observed ratio. The manner

in which the filaments are adjusted to temperature (fast, slow) and the final temperature (high, low) also affect the final observed ratio.

Direct comparison of analyses on the same mass spectrometer are strictly valid only if the sample size, sample composition, mounting procedure, and mass spectrometric filament-heating and data-taking time are identical in all analyses, or are as identical as has previously been determined necessary to preclude them as the limiting factor in the statistical error. Any changes in any of these parameters may introduce significant changes in the total bias which would negate the use of correction factors.

2. Parameter Evaluation

a. Sample Composition and Size

The total composition of the sample generally has an important effect on the ionization efficiency, and the best sample composition must be evaluated by experimentation. This experimentation should be concerned not only with the major extraneous anion or cation, but also with pH, concentration of the element under study, and, in general, total composition of the sample solution. All chemical factors may affect the temperature and efficiency of volatilization and ionization, as well as the work function of the filament material. Even those elements or radicals which are removed during the drying of the sample on the filament are generally important because of their possible effect on the distribution of the dried sample and the sample-filament contact.

Extraneous elements are generally detrimental to the analytical precision of isotopic analyses, and all samples should initially be processed in such a manner so as to give a uniform purity. The practice in this laboratory has been to establish an analytical procedure using the reference sample, usually a very pure salt of the element to be analyzed. The next step is the mineral survey, and the initial chemistry done on the mineral samples is held to a minimum but is uniform

for all samples. As the mineral survey progresses the results from some of the samples usually fall outside the statistical limits of the reference sample. Any sample whose analytical results show a difference is returned to the chemist and carefully repurified, with some effort being made to identify the trace impurities that are removed. By doing the survey in this manner it is possible to identify particularly deleterious impurities and/or to establish the necessary purity for good analytical results. Treating the samples in this manner insures that any difference is real and not the result of some impurity, and in the majority of the elements investigated in this laboratory apparent isotopic differences between samples have disappeared after reprocessing.

b. Filament Material

The usual filament materials are used in this laboratory, and it is the practice of the laboratory to try all of the different filament materials when starting an investigation on a new element. The best filament material and method of ionization (single or multiple filament) for a particular element must be determined experimentally.

The Saha-Langmuir equation may provide a clue as to whether the element in question can be ionized, but in general it has no direct application because the true work function of the contaminated filament surfaces is not known. The elements whose ionization potential is between 7.9 and 11.7 electron volts in general cannot be ionized thermally. There are of course a few exceptions. The filament materials themselves will emit ions of the base element and it is, therefore, possible to observe ions of iridium (I.P. 9.2 V). Boron (I.P. 8.2 V) as a complex ion (meta borate) has a very high ionization efficiency from a platinum or tantalum filament, but, in general a much poorer ionization efficiency from the other filament materials.

Whenever possible, triple-filament sources are to be preferred, since in general they have a higher ionization

efficiency. The increased efficiency will usually allow the analyst to devise an analytical procedure that will minimize the effect of fractionation which will result in a lower rate of change of the ratios with time.

c. Mounting Technique

Since almost all samples are placed on the filaments as solutions or slurries, they must be dried before being inserted into the mass spectrometer. This is usually accomplished by the use of heat lamps and/or electrical currents. The manner in which the samples are dried is very important. Too rapid heating can cause the formation of bubbles or curling of solid material. This will lead to flake-off, or, at least, poor sample-filament contact. For volatile salts, such as bromides and chlorides, the drying temperature must be kept low enough to insure against loss of the element under study, which would change the sample size. For elements which form multiple oxides, it is important to find the best oxide for analyses and to achieve this form in the drying procedure. To this end, it is very helpful to have fiduciary points such as color changes in the sample (see uranium procedure).

In general, since the temperature and manner of drying can affect the physical chemistry of the sample, as well as the physical shape or form of the sample and the sample-filament contact, it is important to mount all samples in an identical manner.

An example of the importance of finding the proper mounting technique can be seen by comparing silver and copper. Both of these elements are mounted as the metal but silver is deposited on the filament as a salt (AgNO_3) and then converted to silver metal by heating in a hydrogen atmosphere, while copper metal is directly electrodeposited on the filament. Although, in both cases, the end result is the metal, the two methods are not interchangeable. Copper which is deposited by converting the salt in a hydrogen atmosphere gives a very

unstable ion beam, and silver which is electrodeposited directly onto the filament does not ionize efficiently.

d. Filament Temperatures and Heating Techniques

Since the integral of time-signal strength is frequently the determining factor in the total bias of the results, it is extremely important to devise and follow a standard technique for all analyses that are to be intercompared.

Filament temperatures which will yield strong, stable ion beams are determined experimentally. Generally, at a sufficiently high temperature, ion beams will first increase in strength, then level off and finally decay. The objective of the experimentation is to determine a filament temperature and heating pattern which gives an extended leveling-off period at an ion current sufficiently large for accurate measurement of all isotopes.

In triple-filament sources, the temperature of the ionizing filament (Re) is monitored by the Re^+ signal. The currents in the sample filaments are separately adjusted so that each contributes 1/2 of the total ion beam which is to be obtained at a specific time in the heating pattern. Specific heating patterns for various elements are discussed in the section on procedures, with some examples that demonstrate that the heating pattern will alter the rate of fractionation thus changing the average bias.

If all samples of an element are prepared and analysed in truly identical manner, they should theoretically have the same ion beam characteristics. However, since slight differences in chemical purity and sample size are always present there will always be variations in the maximum stable ion currents of the analyses. For this reason, the standard signal strength to be used in all analyses should be made low enough (within the bounds of accurate measurement) to be consistently attainable in most analyses. Any individual samples which cannot consistently attain this level of ionization should be chemically re-processed. Also, any

individual analyses which deviate strongly from the general signal pattern of the majority of the analyses should be discarded.

3. Analyses of Particular Elements

a. Introduction

A number of elements have been extensively studied, isotopically, at this laboratory, including Br, Cs, Cl, Cr, Cu, Mg, Pu, Ag, and U. On the following pages are described the chemical and mass spectrometric techniques used for each element. Many details such as voltages, sample size, data-taking period, and standard beam strength are given for each element studied. The general pattern of controlling all parameters is never varied, that is to say that time, temperature, sample size, and preparation are controlled, but the fine details of the procedures are adjusted for each of the elements. The beam strength, in particular, is a direct function of the instrumental efficiency and the element and the signals achieved at this laboratory may be impossible to duplicate with less-efficient instruments, and far too large for instruments equipped with more sensitive detectors. Other details, particularly sample composition and mounting procedures are the results of extensive experimentation and, in general, attempts to mount elements in a common form other than the one described will frequently lead to unusable or inferior ion signals, and/or inferior statistics.

A major purpose in the isotopic analysis of multiple samples is to determine the extent, if any, of natural variations in the isotopic abundances of an element. The correct evaluation of real differences, as opposed to analytically-biased differences, is based on two procedural safeguards.

The first is the continued attempt to maintain absolute uniformity in sample handling and analytical procedure. For some elements this is difficult and as many as 30 to 50% of all analyses attempted are rejected. These analyses are rejected for not maintaining the standard growth, intensity,

or stability pattern and are never calculated. Once a chart has been accepted and calculated the data must be retained. The second safeguard is to reprocess any sample that gives results statistically different from the reference sample. If after the prescribed number of analyses the average isotopic values for a sample are significantly different from the reference values, the sample is chemically re-purified to insure against the possibility that the different analytical results are due to chemical differences. The purified sample is then re-analyzed the prescribed number of times and if it is still significantly different from the reference the difference is considered real.

When real differences are found it is generally useful to re-sample the original "odd" material to determine the characteristics and extent of the isotopic differences. Frequently the differences are confined to surface layers, where they may result from oxidation-reduction phenomena.

1. Analytical Procedure for Bromine

Chemistry

Water-soluble samples, brines, bitters, and sea water are treated as follows: A measured quantity is dissolved in 500 ml of $H_2O + 1 \text{ ml } HNO_3$. The solution is transferred to a distilling apparatus and 50 ml of the solution is distilled into dilute ammonium hydroxide solution, to remove iodine. Seventy-five milliliters of nitric acid are then added and the bromine produced is distilled into dilute ammonium solution. Since chlorine is usually the dominant halide in natural samples, it is necessary to repeat the oxidation and distillation to free the bromine from chlorine. After the second distillation, the solution is made acidic with nitric acid and AgBr is precipitated. The solution is filtered and the precipitate dried in an electric oven ($110^\circ C$). A weighed portion of the AgBr is transferred to a small vial and sufficient concentrated ammonium hydroxide is added so that the resulting solution contains 3 mg Br/ml.

Samples of the mineral bromyrite (AgBr) are dissolved in ammonium hydroxide and the silver is electrodeposited onto a platinum gauze electrode. The solution is then made acidic and treated as in the water-soluble samples.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of the ammoniacal AgBr solution ($60 \mu g \text{ Br}$) is deposited on each sample filament and dried under a heat lamp for 10 minutes. The spacing between ionizing and sample filaments is increased by $1/32$ of an inch. This reduces vaporization of the sample by radiant heat from the ionizing filament but does not appreciably decrease the ionization efficiency.

The Br^- signals are measured at an accelerating voltage of -3780 volts. In all negative thermal ionization work it is necessary to keep the accelerating voltage and ionizing filament temperature low, so as to reduce the source efficiency for electrons.

The draw-out and discriminator plates are set at the average position giving optimal signal strength, determined during the preliminary experiments, and never changed. Results have shown that changing these plates can affect the apparent isotopic ratio. Ionization is probably some combination of thermal ionization and electron impact ionization, with the e^- impact being very minor during a good analysis. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the pressure in the tube is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

Time from start
(minutes)

Procedure

- | | |
|----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0 | The ionizing filament current is set to give a temperature of $\sim 1600^\circ\text{C}$ (~ 3.0 A). The ^{79}Br signal should be < 5 mV. |
| 5 | The sample filament currents are set at 0.5 A. The ^{79}Br signal should be ~ 5 mV. |
| 10 | The sample filament currents are adjusted to give a 10 mV ^{79}Br signal. |
| 15 | The sample filament currents are adjusted to give a 15 mV ^{79}Br signal. At this point the signal should begin to grow slowly. If it has not grown to 25 mV by 30 minutes, the signal is increased to this level by increasing the ionizing filament current. This current should be 3.0 - 3.2 A and must never be raised above 3.4 A because excessive electron emission will occur. The baseline reading is adjusted to zero. |
| 40 | Data-taking begins. The ^{79}Br signal should be 30-40 mV ($3-4 \times 10^{-13}$ A). Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps. |

Bromine signals are easy to control and very stable. All analyses should be made on slowly growing signals. Signals which do not increase by more than 25% during the analyses will not have an observable change in ratio (less than 0.1%) over a 12 minute period.

Notes

The use of NaBr as the sample material leads to erratic Br⁻ signals. The voluminous electrons given off by the sodium overload the field and cause signal instability by changing potentials on plates and defocusing the ion beam.

Attempts to obtain significantly higher beam intensities, as a regular procedure, while maintaining stable signals were not successful. This element, and several others that have a fairly sharply defined maximum signal intensity, can be used to estimate the relative transmission efficiency of different mass spectrometers. Attempts to double or triple the ion intensity will result in a completely different signal pattern, generally a very rapid decay.

In general, background signals are completely negligible but for analyses of highly separated isotopes the ionizing filament should be pre-baked. Also, the analysis of highly-separated isotope sample may have a residual effect on succeeding analyses, so that the source should be thoroughly cleaned after such analyses.

2. Analytical Procedure for Cesium

Chemistry

Cesium nitrate is the salt form used and the final solution is adjusted to 0.1 N HNO_3 and 3 μg Cs/ml.

Mass Spectrometry

A single-filament platinum-ribbon source is used. One drop of solution ($\sim 0.06 \mu\text{g}$ Cs) is placed on the filament and dried under a heat lamp for 10 minutes.

The Cs^+ signals are measured at an accelerating voltage of 10 kV. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the tube pressure is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

<u>Time from start</u> <u>(minutes)</u>	<u>Procedure</u>
0-1	The filament current is set at 1 A.
3	The filament current is adjusted to give a 3 mV Cs grid signal. The signal should grow steadily.
15	The Cs grid signal should have grown to about 30 mV. The filament current is adjusted to give a 150 mV grid signal. The signal should continue to grow.
40	Data-taking begins. The grid signal should have grown to about 300 mV (3×10^{-11} A). Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

All data should be taken on constant or slowly growing signals. In such cases, the observed ratio changes by $< 0.1\%$ over a 30 minute period.

Notes

The onset of cesium emission is very sharp and occurs at a filament current of 1.0 to 1.2 A. The signal grows slowly and steadily but may be erratic; there are momentary gross changes in signal intensity during the first 1/2 hour of heating. The exact cause of this erratic behavior is not known and is not observed during each analysis, but the signal instabilities normally cease before the start of data-taking (40 minutes).

Efforts to get a 150 mV (grid) growing signal may require several temperature adjustments. If the signal decays strongly, wait 2 minutes and readjust the signal to 150 mV. Up to 10 minutes (5 adjustments) are allowed to obtain a growing signal. The Cs emission is very sensitive to small changes in temperature and a cautious approach is used to obtain a growing signal in order to avoid overheating the sample and accelerating the rate of sample depletion. Filament currents of 1.2 to 1.4 A are normally sufficient to give the required signal.

The filaments are prebaked at 2.2 A for 1/2 hour in a vacuum and under a potential field, to eliminate the possibility of barium background signals from the filament material.

Single-filament platinum-ribbon sources give far more efficient ionization of cesium than do single-filament rhenium, tungsten, and tantalum, or triple-filament rhenium-ribbon sources. With a platinum filament, the sample size can be small enough so that very radioactive samples may be analyzed without undue hazard to the analyst or excessive contamination of the mass spectrometer.

No extensive study of Cs minerals has been made at this laboratory; only occasional service analyses.

3. Analytical Procedure for Chlorine

Chemistry

The natural samples, halite and sylvite, are dissolved in H_2O . A few drops of nitric acid and an excess of silver nitrate are added. The precipitated silver chloride is allowed to stand in the dark overnight. The solution is filtered through a fine-porosity porcelain filter and the precipitate is washed with distilled water. The silver chloride is weighed (in the filter), dissolved in 1 ml of concentrated ammonium hydroxide and drawn through the filter into a small vial. The filter is washed twice with 0.5 ml of ammonium hydroxide. The final solution is adjusted to 15 mg Cl/ml by adding the appropriate amount of concentrated ammonium hydroxide.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of ammoniacal silver chloride solution ($\sim 300 \mu g \text{ Cl}$) is placed on each sample filament and dried in the following manner: 5 minutes with heat lamps only; 2 1/2 minutes at 1 A; 2 1/2 minutes at 1.5 A. The current is then increased until the deposit flows and then redrys (1.8 - 2.0 A). The spacing between ionizing and sample filaments is increased by 1/32 of an inch. This reduces vaporization of the sample by radiant heat from the ionizing filament but does not appreciably decrease the ionization efficiency.

The Cl^- signals are measured at an accelerating voltage of -3780 volts. In all negative thermal ionization work it is necessary to keep the accelerating voltage and ionizing filament temperature low so as to reduce the source efficiency for electrons.

The draw-out and discriminator plates are set at the average position giving optimal signal strength, determined during the preliminary experiments, and never changed. Results have shown that changing these plates can affect the apparent isotopic ratio. Ionization is probably some

combination of thermal plus electron impact, with the e^- impact being very minor during a good analysis. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the pressure in the tube is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

<u>Time from start</u> <u>(minutes)</u>	<u>Procedure</u>
0	The ionizing filament current is set to give a Cl grid signal of 1/2-1 mV (~ 3.2 A).
3	The sample filament currents are set at 0.5 A. The ^{35}Cl signal should be ~ 10 mV.
5	The sample filament currents are increased to give a ^{35}Cl signal of 150 mV. The signal will generally decay to about 100 mV in the next few minutes.
10	The sample filament currents are adjusted to give a ^{35}Cl signal of 150 mV. At this point the signal will begin to grow and should continue to grow steadily for the remainder of the analysis.
25	The ^{35}Cl signal should have grown to 250-300 mV. If not, it is increased to 250 mV (2.5×10^{-12} A) by raising the sample filament currents. Baseline readings are taken.
40	Data-taking begins. The ^{35}Cl signal should be ~ 350 mV. Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

Notes

The use of NaCl as the sample material leads to erratic Cl^- signals. The voluminous electrons given off by the sodium overload the field and cause signal instability by changing potentials on plates and defocusing the ion beam.

Chlorine ions are virtually the only background signal in the negative ion spectrum and, though small, the background interferes with the analyses of the separated isotopes. The method used to circumvent this problem was to use the same set of filaments over and over until the background spectrum of these filaments approached that of the separated isotopes.

Also the analysis of a highly separated isotope sample may have a residual affect on succeeding analyses, so that the source should be thoroughly cleaned after such an analysis.

4. Analytical Procedure for Chromium Chemistry

Chromite and Cr-Silicate samples are crushed and fused with sodium carbonate. The melt is dissolved in an excess of dilute perchloric acid and the solution is evaporated at 140-150°C until fuming begins. This precipitates the silica and oxidizes the Cr (III) to Cr (VI). After filtration, the solution is adjusted to pH 8 with ammonium hydroxide and hydrogen peroxide is added to insure complete oxidation of the chromium. The solution is then filtered to remove insoluble hydroxides, and sulfurous acid is added to reduce the Cr (VI) to Cr (III) and thus cause precipitation of $\text{Cr}(\text{OH})_3$. The $\text{Cr}(\text{OH})_3$ is filtered, ignited to Cr_2O_3 at 800°C, and weighed. The Cr_2O_3 is taken into solution by digestion with perchloric acid at 140-150°C. Sulfurous acid is then added to reduce the Cr (VI) to Cr (III) and $\text{Cr}(\text{OH})_3$ is precipitated by adjusting to pH 8 with dilute ammonium hydroxide. The $\text{Cr}(\text{OH})_3$ is caught on a filter and dissolved in hot HNO_3 (1 + 9). This solution is evaporated to dryness and the residue is dissolved in an amount of HNO_3 (1 + 99) so that the Cr concentrated in 3 mg/ml.

Two minerals are taken into solution by other methods. Crocoite (PbCrO_4) is dissolved in perchloric acid, the lead is removed by electrodeposition, and the chromium is precipitated as above. Merumite ($\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is dissolved in hot perchloric acid at 140-100°C and treated as above.

Mass Spectrometry

A single-filament platinum-ribbon source is used. The sample is mounted in the following manner: A drop of solution ($\sim 60 \mu\text{g Cr}$) is placed on the filament and dried with a heat lamp and 1.3 A of current for 5 minutes; the current and lamp are turned off and a drop of 10% HNO_3 or distilled water is placed on the filament; the sample is then re-dried with the heat lamp and a current of 1.2 A for 5 minutes; 1.6 A for 1 minute, and 2.2 A for 1 minute. The drop of acid or water

serves to spread the sample evenly on the filament; the two reagents appear to work equally well.

The Cr^+ signals are measured at an accelerating voltage of 10 kV on the 12-inch mass spectrometer and 7.75 kV on the 6-inch mass spectrometer. The source and collector slit openings are 7 and 40 mils, respectively, for the 12-inch instrument and 6 and 30 mils, respectively, for the 6-inch instrument. Analyses are begun when the tube pressure is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

<u>Time from start</u> <u>(minutes)</u>	<u>Procedure</u>
0-1	The filament current is set at 2.2 A. The ^{52}Cr signal is found and focused.
2	The filament current is increased to 2.3 A.
4-14	The filament current is increased 0.1 A every 2 minutes until the Cr signal begins to grow rapidly.
10-15	The ^{52}Cr signal should have grown very rapidly. When it reaches 20 V, the filament current is reduced so that $^{52}\text{Cr} = 2$ V (generally 2.0 - 2.3 A).
15-25	The signal should grow slowly. It is kept between 2 and 3 V by appropriate adjustment of the filament current.
25	The final filament current adjustment is made to give a ^{52}Cr signal of 2 V. Baseline readings are taken.
37	Data-taking begins. The ^{52}Cr signal should be 2-3 V and slowly growing. Each of the three less abundant isotopes is measured relative to the ^{52}Cr isotope. Groups of four results are obtained for each ratio in the following sequence: 50/52, 53/52, 54/52, 53/52, 50/52 giving 8 results for the 50/52

and 53/52 ratios and 4 for the 54/52 ratios. Since the sequence is symmetric any changes due to fractionation will balance out and no secondary time dependent bias is introduced between the minor isotopes. The Cr signal should increase slowly but steadily throughout the data-taking period (20-25 min.). Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

With a stable or slowly growing signal, the 50/52 ratio will generally decrease by $\sim 0.1\%$ during the data-taking period (20-25 min.). However the observed ratio may change much more rapidly if a decaying signal is used.

Notes

If large amounts of the alkali elements are present in a sample, they will inhibit the ionization of the chromium and the chromium signal will not grow until the alkali ion signals have degraded to a reasonable level.

A number of different mounting procedures were tried, including drying in air to a green oxide, drying in air to a black oxide, drying in an O_2 atmosphere, and drying in a H_2 atmosphere, all without the 10% HNO_3 (or H_2O) drop. All of these procedures lead to poor sample-filament contact and generally resulted in erratic analyses.

Very strong (> 20 V) ^{52}Cr signals may be obtained quite easily but such signals are generally erratic, decay rapidly, and are difficult to standardize.

Triple-filament Re sources give strong, stable Cr signals but are unusable because of a large Cr background signal from the high temperature ionizing filament. In addition, when the side filaments or triple filament sources are heated hot enough to vaporize the chromium they also give a strong ion beam.

All filaments are prebaked at 2 A for 1 hour in a vacuum and under a potential field.

5. Analytical Procedure for Copper

Chemistry

A weighed quantity (1 to 3 gm) of mineral is treated with dilute (1:2) HNO_3 and digested overnight on a steam bath. The solution is filtered and evaporated to dryness, and the residue is dissolved in 75 ml of an aqueous solution containing 1 ml of HNO_3 and 1 ml of H_2SO_4 . The copper is electro-deposited onto a platinum gauze cathode at a current of about 0.2 A. The cathode is then removed and washed with water while the smaller platinum gauze anode is cleaned with dilute HNO_3 and H_2O_2 to remove any oxides of lead and manganese which may have been deposited. The original electrolyte is discarded and replaced with a fresh batch. The polarity of the electrodes is reversed so that the original cathode becomes the anode, and the copper is electrolytically stripped from the anode and deposited on the cathode. The cathode is then removed, washed with water, dipped in ethanol, and dried for 1 minute at 105°C . The weight of the copper is determined from the weight of the electrode before and after deposition. The copper is dissolved from the electrode with dilute HNO_3 and the solution is evaporated to dryness. The residue is redissolved in dilute HNO_3 and the solution is brought up to a volume so that the copper concentration is 10 mg/ml.

Samples whose mass spectrometric results indicate the need for further purification are treated as follows: The sample solution is mixed with dilute (1:2) HNO_3 and heated overnight on a steam bath. The solution is filtered and the filtrate is evaporated to dryness. The residue is dissolved in dilute HCl and re-evaporated to dryness to remove HNO_3 . The residue is then dissolved in 100 ml of 1N HCl and the copper is precipitated with H_2S . After filtration, the precipitate is dissolved in dilute HNO_3 , evaporated to dryness, dissolved in HCl and re-dried again to remove the HNO_3 . The residue is dissolved in dilute HCl and the solution is made ammoniacal, filtered, and treated with H_2S . The solution is

then filtered and the precipitate of CuS is ignited to CuO at 500°C. The CuO is dissolved in dilute HNO₃ and the solution is evaporated to dryness. The residue is dissolved in dilute HNO₃-H₂SO₄ solution and the copper is electrodeposited once, with the final solution being prepared as described above.

For samples in which the copper concentration is low, the copper is first concentrated by precipitation with H₂S and then purified by the electrodeposition method described above.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution is placed on each sample filament and the copper is electrodeposited onto the filament. Platinum wire is used as the anode. The potential difference is 3 1/2 volts and a 1 ma current is passed through the solution for 5 minutes. The estimated sample size is 200 µg Cu per sample filament. The spacing between ionizing and sample filaments is increased by 1/32 of an inch to reduce sample evaporation by radiant heat from the 2100°C ionizing filament.

The Cu⁺ signals are measured at an accelerating voltage of 10 kV. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the tube pressure is < 4 x 10⁻⁷ torr.

The following analytical procedure is used:

Time from start
(minutes)

Procedure

- | | |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0-1 | The ionizing filament current is set to give a 50 mV Re grid signal (5-6 A). The sample filament currents are set at 0.5 A, while the Re signal is being monitored. |
| 4-6 | If necessary, the ionizing filament current is readjusted to give a 50 mV Re grid signal. The sample filament currents are slowly increased until the Cu signal is detectable. The ⁶³ Cu peak is located and focused. The sample |

filament currents are adjusted to give a 6 mV ^{63}Cu signal (0.8 - 1.0 A).

- 12 The sample filament currents are adjusted to give a 30 mV ^{63}Cu signal. The signal may decay for a brief period but should then begin to grow slowly ($\sim 1 \text{ mV/min.}$).
- 18 If the ^{63}Cu signal has not grown to at least 35 mV, the sample filament currents are increased to obtain this intensity. The signal should continue to grow slowly and no further adjustments should be made.
- 25 Data-taking begins. The ^{63}Cu signal should be 40-50 mV. Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

All data should be taken only on constant or growing signals. Under these conditions the observed ratio does not change with time. Data taken on rapidly decaying signals may show a rapid change in observed ratio with time.

Notes

During the first 12 minutes of heating the primary objective is to allow the ion source to warm up and approach thermal equilibrium. The temperature of the ionizing filament is approximately 2100°C and is hot enough for efficient ionization but cool enough so that radiant heat effects are negligible.

The accumulation of copper on the ion source during the normal lifetime of 30 to 40 sample-loadings is not large enough to cause memory or give a detectable source background signal. The rhenium filaments contain a minute quantity of copper which gives a Cu^{+} current of less than $1 \times 10^{-16} \text{ A}$ at 2100°C , and is detectable only with an ion multiplier. Only after extensive periods of baking is it possible to reduce the filament background signal to zero intensity.

Of all the isotopic ratios of elements studied at this laboratory, the copper ratio is probably the most sensitive to variation in analytical technique or heating pattern. For careful work the 95% confidence limit of a single determination is 0.15% of the ratio. The average long-term observed $^{63}\text{Cu}/^{65}\text{Cu}$ ratio is 2.2750, but ratios 1 to 2% lower than this value can be consistently obtained by simply overheating the filaments or changing the time-signal strength relationship. Failure to adhere to a strict time-signal strength relationship can lead to a significant expansion of the analytical limit of error, thereby eliminating the possibility of detecting small but real differences in the copper isotope ratios of various minerals. It was not possible to routinely obtain stable signals greater than 50 mV (5×10^{-13} A).

This element, and several others that have a fairly sharply defined maximum signal intensity, can be used to estimate the relative transmission efficiency of different mass spectrometers. Attempts to double or triple the ion intensity will result in a completely different signal pattern, generally a very rapid decay.

6. Analytical Procedure for Magnesium

Chemistry

Acid soluble materials are taken into solution with dilute hydrochloric acid. Silicate materials are fused with sodium carbonate before being dissolved in dilute hydrochloric acid. The magnesium is purified and recovered by a variation of the method of Bricker and Parker⁽¹⁾. An ammoniacal solution of (ethylenedinitrilo) tetraacetic acid is used to precipitate the magnesium as magnesium dihydrogen (ethylenedinitrilo) tetraacetate hexahydrate ($\text{MgC}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 6\text{H}_2\text{O}$). A double precipitation is used to insure the removal of sodium which would present a major problem in the mass spectrometry.

Although the recovery of magnesium, by this procedure, is high (>95%), it is not quantitative; about 0.5 mg of magnesium is left in solution when ~10 mg of magnesium is precipitated. However mass spectrometric examination has shown that the isotopic composition of the magnesium left in solution is identical with that of the precipitated magnesium, so there is no significant fractionation during the sample preparation.

The magnesium complex is ignited to MgO at 1000°C and dissolved in dilute HCl. Since pure MgO does not adhere well to rhenium filaments some uranyl nitrate is added to the solution to act as a binding agent. The final solution contains 5 mg Mg/ml + 5 mg U/ml and 10% HNO_3 .

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution (~100 µg Mg) is placed on each sample filament and dried with a heat lamp and an electrical current which is increased until the uranium forms an orange oxide. The electrical current is adjusted in the following manner:

(1) Bricker, C. E. and Parker, G. H., Anal. Chem. 29, 1470-1474, (1957).

1.5 A for 5 minutes; 1.8 A for 1/4 minute; slowly increased (period of $\sim 1/2$ min.) until orange uranium oxide forms (2.0 - 2.5 A).

One internal modification is made on the 12-inch mass spectrometer, for Mg analyses. The opening of the first baffle on the collector is narrowed to $5/8$ ". Since the masses are about $1/2$ " apart in this mass range, a 1" opening puts the ^{23}Na peak on the edge of the baffle when the ^{24}Mg is being collected, causing troublesome edge-effects.

The Mg^+ signals are measured at an accelerating voltage of 8000 volts*. Higher voltages will increase the size of the Mg^+ signal but will also greatly increase the number of secondary electrons from the Na^+ beam with consequent deleterious effects on the baselines under the Mg^+ peaks. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the tube pressure is $< 2 \times 10^{-7}$ torr.

The following analytical procedure is used:*

<u>Time from start (minutes)</u>	<u>Procedure</u>
0-1	The ionizing filament current is adjusted to give a 100 mV Re grid signal (~ 6 A, $T \approx 2100^\circ\text{C}$).
1	The sample filament currents are set at 2.4 A while the Re signal is being monitored.
4	The ionizing filament current is readjusted to give a 100 mV Re grid signal.
5	The ^{24}Mg signal is found and focused on. If this signal is > 200 mV the sample filament currents are lowered and then readjusted so that each one gives 75 mV of ^{24}Mg signal.
10	The sample filament currents are adjusted to give a 200 mV ^{24}Mg signal. The signal will generally grow slowly.

* For the 6-inch instrument.

- 15 The sample filament currents are adjusted to give a 400 mV ^{24}Mg signal. The signal will increase slowly for the remainder of the analysis.
- 20 Baseline readings are taken.
- 27 Data-taking begins. Ten peak sets are taken over the next 20-25 minutes. A complete peak set includes five mass peaks: 24-25-26-25-24, with each interior ^{24}Mg peak being the last and first peak of successive sets. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

There is significant fractionation during the mass spectrometric analysis. Over a 25 minute period, the $^{24}\text{Mg}/^{26}\text{Mg}$ ratio will usually decrease by approximately 0.5%. In view of this it is very important to follow a strict time schedule of filament heating and signal strength and to restrict the data-taking to a particular time interval. It is generally possible to obtain growing signals in all Mg analyses, and such signals have relatively slow rates of change in observed ratios with time. However, rapidly decaying signals usually have rapidly changing observed ratios and such analyses should always be discarded; they invariably give results which are low in ^{24}Mg .

When a 12-inch instrument is used for magnesium analysis the Re grid signal is set at 75 mV and Mg^+ signals obtained at the various stages are only 1/2 those obtained with the 6-inch instrument. For magnesium the 6-inch instrument is approximately twice as efficient as the 12-inch instrument and although 400 mV signals can be obtained with a 12-inch instrument they are generally decaying and a high percentage of the analyses are unusable.

Notes

Attempts to mount the magnesium from chloride and nitrate solutions with no uranium lead to erratic (and abortive) results because of frequent partial or complete flake-off. Analyses using 1-5% HNO_3 solutions (with uranium) did not have the signal stability attained when 10% HNO_3 was used.

The center filaments are always prebaked (1/2 hr. at 5 A) in a vacuum and under a potential field (300 V) to reduce the background Na signal from the Re ribbon. Aside from an alcohol wash, the sample filaments are not pretreated in any manner; prebaked sample filaments increase the likelihood of flake-off. The background signal of the entire filament set-up is negligible, being virtually non-existent ($< 1 \text{ mV } ^{24}\text{Mg}$).

A small amount ($\sim 1\%$) of source memory can sometimes be detected if samples of widely different isotope composition are analyzed back to back on the same source. The memory appears to occur only after an analysis in which particulate sample matter has flaked-off the filaments and adhered to the source plates. The succeeding analyses then may show memory of the flaked-off sample.

It is of primary importance to keep the sodium signal at a minimum. Although there is no problem at all in resolving the ^{23}Na and ^{24}Mg peaks, the scattering of secondary electrons produced by the Na^+ beam can cause sharp and significant depressions in the baselines under the ^{25}Mg and ^{26}Mg peaks. The Na^+ signal is minimized by careful chemistry and by prebaking the ionizing filament. The effects of the small but invariably present Na^+ beam are made negligible by restricting the size of the baffle and by the use of the usual, but in this case particularly important, suppressor grids in the collector.

7. Analytical Procedure for Plutonium

Chemistry

Plutonium sulfate tetrahydrate is prepared from high-purity metal. Any americium present in the sample is removed by the use of a small column of Dowex 1 x 4 ion-exchange resin. An 8 N nitric acid solution of the sample is put through the column and the plutonium is absorbed while the americium is not. The plutonium is then stripped from the column with 0.3 N nitric acid and the final solution is adjusted to 0.1 mg Pu/ml, in 2N HNO₃.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution (~ 2 μ g Pu) is placed on each sample filament and dried by the use of a heat lamp and an electrical current. The current is adjusted in the following manner: 1 A for 5 minutes; 1.2 A for 3 minutes; slowly increased to approximately 2 A, over a 1 minute period, to convert the plutonium sulfate to plutonium oxide.

The Pu⁺ signals are measured at an accelerating voltage of 10 kV. The source and collector slit openings are 7 and 25 mils, respectively.

After the sample is loaded into the mass spectrometer and a pressure $< 4 \times 10^{-7}$ torr is achieved, the filaments are heated in order to dehydrate the sample and eliminate this source of oxygen, which would otherwise lead to the formation of a strong PuO⁺ signal. The dehydrating procedure is as follows: The ionizing filament current is adjusted to give a rhenium grid signal of 70 mV. The sample filament currents are set to give a Pu grid signal of 40 mV. All filaments are left on for 10 minutes, and then turned off and allowed to cool for at least 20 minutes. Analyses are begun when the tube pressure is $< 1 \times 10^{-7}$ torr.

The following analytical procedure is used:

Time from start
(minutes)

Procedure

- | | |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0-1 | The ionizing filament current is adjusted to give a 100 mV Re grid signal. (The corresponding ^{187}Re signal is 650 mV). The sample filament currents are set at 1.4 A. The Pu signal is usually not detectable. |
| 5 | Check the focus of the rhenium signal. The Re signal will usually decay during the first few minutes of heating, so the ionizing filament current is readjusted to give a 650 mV ^{187}Re signal. |
| 6 | The sample filament currents are increased until the Pu signal is located and then adjusted to 40 mV grid. |
| 11 | Check the ^{187}Re signal intensity and, if necessary, adjust to 650 mV. |
| 12 | The sample filament currents are increased to give an 80 mV Pu grid signal. |
| 18 | The sample filament currents are increased to give a 120 mV Pu grid signal. |
| 24 | The signal should be between 120 and 150 mV and growing slowly. No further adjustments should be made. |
| 30 | Data-taking begins. The Pu grid signal should be approximately 150 mV and nearly constant. Ratio determinations are made in the following order: |

1. $^{239}\text{Pu}/^{240}\text{Pu}$
2. $^{240}\text{Pu}/^{241}\text{Pu}/^{242}\text{Pu}$
3. $^{239}\text{Pu}/^{240}\text{Pu}$

Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

The $^{239}\text{Pu}/^{240}\text{Pu}$ ratio will usually decrease by about 0.1% over a 30 minute period.

Notes

The behavior and characteristics of plutonium analysis are similar to that of uranium analysis. The temperature of the sample filament for plutonium analyses (2.0 - 2.3 A) is slightly lower than that for uranium analysis, and can be controlled for both low and high temperature analyses.

8. Analytical Procedure for Silver

Chemistry

The sample is dissolved in nitric acid. The solution is filtered and the silver is precipitated as silver chloride. The dried silver chloride is placed on a layer of sodium carbonate in a porcelain dish, and is reduced to metallic silver by directing a gas-oxygen flame on it from above. The metal is washed free of sodium carbonate and dissolved in nitric acid. The solution is adjusted to a concentration of 10 mg of silver per ml of 1:25 nitric acid.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution ($\sim 200 \mu\text{g Ag}$) is placed on each sample filament and dried with a heat lamp and an electrical current of 1 A for 5 minutes, in air. The sample is then converted to metallic silver by placing the filament in a hydrogen atmosphere and increasing the electrical current until the filament begins to glow red (2.0 - 2.8 A). The spacing between ionizing and sample filaments is increased by $1/32$ of an inch to inhibit sample evaporation by radiant heat from the white-hot ionizing filament.

The Ag^+ signals are measured at an accelerating voltage of 10 kV. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the tube pressure is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

<u>Time from start</u> <u>(minutes)</u>	<u>Procedure</u>
0-1	The ionizing filament current is set to give a ^{187}Re signal of 650 MV. The sample filament currents are set at 0.25 A.
3-4	The ionizing filament current is readjusted to give a ^{187}Re signal of 650 mV. ^{107}Ag is located and the sample filament currents are increased to give a ^{107}Ag signal of 70 mV

(7×10^{-13} A). During the next few minutes the signal may decay at first but should then begin to grow.

15 The sample filament currents are increased to give a ^{107}Ag signal of 120 mV (1.2×10^{-12} A). The signal should continue to grow.

20 Data-taking begins. The ^{107}Ag signal should be stable at ~ 150 mV. Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

Under the above conditions the $^{107}\text{Ag}/^{109}\text{Ag}$ ratio will generally decrease by about 0.25% over a 20-minute period.

Notes

If large signals are not necessary it is possible to use 200 μg (total) samples and reduce the sample filament temperatures to give 30 to 50 mV signals which will grow slowly throughout the analyses. Under these conditions the ratio will not change with time ($< 0.1\%$).

With very small samples ($< 5 \mu\text{g}$), the above procedure must be modified. The desired signal strength is achieved sooner and data-taking is begun after only 15 minutes. Generally, when very small samples are used the signal will grow, level off, and decay very rapidly, so the time schedule must be condensed.

Care must be taken not to overheat the sample filaments. If they are overheated the signal will grow rapidly and then decay rapidly, giving rise to rapidly changing observed ratios. Once the decay process has begun, cooling the filaments will not suspend it.

Attempts to analyze silver as the nitrate, sulphide, and chloride, without converting it to metallic silver, were not successful.

Significant amounts of zirconium, either in the filament or the sample, can lead to the formation of a zirconium oxide ($^{91}\text{Zr}^{16}\text{O}$) background signal at the 107 mass position, as well as at the 106, 108, 110, and 111 mass positions. Baking out the filament eliminates the zirconium from the source, but if zirconium is present in the sample in significant amounts it is sometimes impossible to reduce the mass 107 zirconium oxide signals to a negligible value before the data-taking period begins.

9. Analytical Procedure for Uranium

Chemistry

Uranium standards, as U_3O_8 , are dissolved in dilute nitric acid (1:1) and the final solutions are adjusted to contain 5 mg of uranium per milliliter, in 5% nitric acid.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution (100 μ g U) is placed on each sample filament and dried with a heat lamp and an electrical current. The electrical current is adjusted as follows: 1 A for 5 minutes; 1.2 A for 3 minutes; slowly increased (period of 1 minute) until the yellow-orange oxide forms (1.8 - 2.5 A). Heating too quickly may cause the sample to flake-off. Overheating the filament will convert the sample to a black uranium oxide, which is to be avoided since the yellow-orange oxide generally gives superior performance.

The U^+ signals are measured at an accelerating voltage of 10 kV. The source and collector slit openings are 7 and 25 mils, respectively. The sample is degassed for 10 minutes and then allowed to cool and pump down for at least 30 minutes before the actual analysis is begun. The primary purpose of the degassing step is to dehydrate the sample. This eliminates a source of oxygen which would otherwise lead to the formation of a large UO^+ signal. A secondary function of degassing is to drive-off uranyl nitrate that is not converted to UO_3 during sample preparation. The magnitude of this signal at low sample filament temperatures (1.5 to 2.0 A) is occasionally greater than 5×10^{-11} A, but is decaying too fast for a precise ratio determination. Degassing is begun when the tube pressure is 4×10^{-7} torr. An accelerating voltage of 8 kV is used, to decrease the likelihood of high voltage breakdown during the first few minutes of heating, when large amounts of volatile material are driven off.

The signal strength necessary for a precise analysis is determined by which isotopic ratios are to be measured. The ^{235}U and ^{238}U abundances generally amount to at least 98% of the total sample and if only a $^{235}\text{U}/^{238}\text{U}$ ratio is to be measured, a total uranium signal of 3×10^{-11} A is sufficient. Such an analysis is called a "low-temperature" analysis and requires sample filament currents of 2.2 to 2.5 A, with a corresponding uranium grid signal of 0.3 volts.

Precise determination of the isotopic abundances of all uranium isotopes in a sample requires a large ion current ($1-4 \times 10^{-10}$ A), since the individual ^{234}U and ^{236}U abundances are usually less than 1%. Such an analysis is called a "high-temperature" analysis and requires sample filament currents of 2.6 to 3.0 A, with a corresponding uranium grid signal of 1.2 volts (4 volts on instrument equipped with Z lens).

The following analytical procedure is used:

Degassing of Samples

<u>Time from start (minutes)</u>	<u>Procedure</u>
0-1	The ionizing filament current is adjusted to give a detectable Re grid signal. The ^{187}Re peak is located and focussed. The ionizing filament current is adjusted to give a 600 mV ^{187}Re signal. The sample filament currents are set at 1.5 A.
3-4	Check the focus of the rhenium signal. If necessary, the ionizing filament current is readjusted to give a 600 mV ^{187}Re signal. The uranium is found and the sample filament currents are increased to give a 100 mV U grid signal. This signal will usually decay during the degassing step.
10	All filaments are turned off.

Low-Temperature Analysis

- 0-1 The ionizing filament current is adjusted to give a detectable Re grid signal. The sample filament currents are set at 1.5 A. The ^{187}Re peak is located and focused for maximum intensity. The ionizing filament current is then adjusted to give a 650 mV ^{187}Re signal. The corresponding Re grid signal is ~ 100 mV and the filament temperature is $\sim 2150^\circ\text{C}$. The uranium signal will usually be less than 3×10^{-13} A.
- 5 Check the focus of the rhenium signal. The Re signal will usually decay during the first few minutes of heating so the ionizing filament current is readjusted to give a 650 mV ^{187}Re signal. The U signal is located.
- 6 The sample filament currents are increased to give a 100 mV U grid signal.
- 11 Check the ^{187}Re signal intensity and, if necessary, adjust to 650 mV.
- 12 The sample filament currents are increased to give a 200 mV U grid signal.
- 18 The sample filament currents are increased to give a 300 mV U grid signal.
- 24 If the signal intensity has changed significantly (± 50 mV), the sample filament currents are readjusted to give a 300 mV U grid signal.
- 30 Data-taking begins. The U grid signal should be approximately 300 mV. Ten scan sets are taken. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

High-Temperature Analysis

- 0-1 The ionizing filament current is adjusted to give a detectable Re^+ grid signal. The sample filament currents are set at 1.5 A. The ^{187}Re peak is located and focused for maximum intensity. The ionizing filament current is then adjusted to give a 650 mV ^{187}Re signal. The corresponding Re grid signal is ~ 100 mV and the filament temperature is $\sim 2150^\circ\text{C}$. The uranium signal will usually be less than $3 \times 10^{-13}\text{A}$.
- 5 Check the focus of the Re signal. The Re signal will generally decay during the first few minutes of heating, so the ionizing filament current is readjusted to give a 650 mV ^{187}Re signal. The U signal is located.
- 6 The sample filament currents are increased to give a 600 mV U grid signal. (Sample filament currents approximately 2.5 - 2.7 A).
- 11 Check the ^{187}Re signal intensity and, if necessary, adjust to 650 mV.
- 12 The sample filament currents are increased to give a 1.2 volt U grid signal. The signal will generally decay during the next few minutes. However, if it should grow, or decay and then grow, it should not be allowed to exceed 1.2 volts.
- 18 If the signal intensity has changed significantly (± 200 mV), the sample filament currents are readjusted to give a 1.2 volt U grid signal.
- 24 If the U grid signal is ~ 1.1 volts and is constant, slightly growing or decaying, no further adjustments are necessary.

Data-taking begins. Seven peak sets of $^{235}\text{U}/^{238}\text{U}$ are taken first; each peak monitored for 1/2 minute and magnet changes are made in discrete steps. Then $^{234}\text{U}/^{235}\text{U}$ and $^{236}\text{U}/^{235}\text{U}$ ratios are determined by continuous mass scanning, which is necessary for the accurate measurement of baselines under the small peaks. Ten peak sets are taken. Finally another 7 peak sets of $^{235}\text{U}/^{238}\text{U}$ are taken, as before.

Less than 5 minutes are normally required to obtain a constant ^{187}Re signal of $6.5 \times 10^{-12}\text{A}$. Provision is made in the analytical procedures for filaments that require more than 5 minutes to yield a constant Re ion current. The intensity and constancy of the Re signal for such filaments must always be checked before the sample filaments are adjusted to yield more intense signals. If the ^{187}Re signal intensity is not constant or slowly changing between 6×10^{-12} and $7 \times 10^{-12}\text{A}$ after 18 minutes of heating, the analysis is discarded. When the ^{187}Re signal is significantly outside this range, the ionizing filament temperature is either too hot or too cool. This means that the sample filaments temperature will have to be too cool or too hot, in order to obtain the standard signal intensity. The net effect of this temperature compensation will be to decrease the precision of the measurements.

The uranium signal has been observed to go through a growth cycle shortly after a significant signal is obtained. This growth cycle is, in most cases, less than 10 minutes in duration. After the growth cycle, there may be a period of short duration when the signal is constant. This cycle is followed by decay. Continued adjustment of the sample filaments will improve the slope of the decaying signal but does not cause an immediate reversal to the growth cycle. During

periods of extensive high-temperature work, the U^+ signal decayed most of the analytical time (approximately 1 1/2 hours) before approaching a constant intensity. Occasionally, the signal will decay, stabilize, and grow during data-taking for high-temperature analysis. The behavior (growing, constant, or decaying) of the uranium signal is not attributed to sample size since only a small portion of the total sample (200 μ g) is used for analysis.

The U^+ signal will normally decay for most high-temperature and low-temperature analyses. The isotopic ratios are, within the limits of analytical precision, independent of signal behavior with the possible exception of rapid and long-term growth. Strongly growing signals during data-taking are rare and can be considered a good indication of overheating for the particular technique used and the isotopic ratios are likely to show the effect of increased fractionation. If the signal is decaying during data-taking, the limiting factor is the ability of the analyst to accurately plot and read peak-heights with the expanded scale recorder. Therefore, if there is excessive growth or decay, the analysis is discarded.

Notes

Uranium has been analyzed more extensively than any other element at this laboratory. We now have the ability to control the bias for long periods of time (6 months or more) with consistent average biases of 0, .15%, .25%, .3%, and .5%. This assortment of biases is due to different combinations of mass spectrometric, analytical and chemical parameters. The full effect of all parameters associated with uranium analyses by thermal emission mass spectrometry is not completely understood, but it has been possible to identify some of the sources of bias and show that they can be controlled, at the 0.1% level for extended periods.

Since the installation of an expanded-scale recorder in the measuring circuit, and the improved collector, all

identified bias components are associated with the filaments, except when the spectrometer is equipped with an ion multiplier. This filament bias is dependent upon the sample size, sample purity, temperature of the filament system, physical chemistry at the filament surfaces, acidity of the solution, and the time-signal strength relationship. Gross changes in transmission efficiency have the effect of requiring a temperature compensation to yield a standard signal intensity; therefore, malfunctions or defocused conditions which reduce transmission are likely to affect the rate of fractionation of the uranium isotopes, and a significant difference is reflected in the experimental ratios measured under these conditions, when compared with experimental ratios measured under focused conditions.

Variation of uranium isotopic ratios with time is related to the rate of depletion of the sample which is, to a large extent, controlled by the temperature of the filament system. The temperature of the ionizing filament for all analyses is approximately 2150°C. The ^{187}Re ion current from a 2150°C filament is approximately 6.5×10^{-12} A and is used as a fiduciary for making a direct and accurate temperature setting of the ionizing filament. This temperature was selected because it is high enough for efficient triple-filament ionization and can be maintained at 2150°C for long periods of time without danger of burning-out the filament; a lower ionizing filament temperature will not drive out the interstitial O_2 which is one of the sources of a UO^+ ion beam.

Since the ionizing filament is maintained at a nearly-constant temperature which does not cause serious sample depletion, the temperature of the sample filaments becomes an all important parameter. Sample size, purity and acidity of the solution all have some effect on the temperature necessary to obtain a standard signal. The magnitude of these effects as reflected by the sample filament currents,

is 0.3 A or less. Impure samples generally require higher temperatures than pure samples to produce a standard signal intensity. Significant increases in the sample size require lower than normal temperatures to yield a standard signal intensity.

Data are given in Tables 1a and 1b showing the results of a preliminary study of uranium solutions of variable sample size and acidity. The NBS U500 standard was put into solution in concentrations of 1, 5, and 10 milligrams of uranium per milliliter. For each concentration there was a neutral solution and acid solutions containing 1%, 5%, and 10% HNO_3 . Each of the 12 solutions was analyzed under low-temperature and high-temperature conditions with separate sample loadings for each technique. Statistical analysis of the data shows that any differences between the averages of two sample sizes that exceed 0.000405 can be considered as significant at the 95% confidence level. Similarly, any differences between the averages of two acidity levels that exceed 0.000530 can be considered as significant at the 95% confidence level.

For low-temperature data it can be seen that:

1. The results for the 400 μg sample size are higher than those of the smaller sizes.
2. The results for neutral solutions are lower than those for acid solutions.

For high-temperature data it can be seen that:

1. The results for the 40 μg sample size are lower than those of the larger sample sizes.
2. There are no differences in results for the lower acidity levels.

Table 1a. Low-Temperature Data
Acidity/Sample Size Experiment

Experimental $^{235}\text{U}/^{238}\text{U}$ Ratios for U500 Standard

	40 μg	200 μg	400 μg	Average
	<u>Sample size</u>	<u>Sample size</u>	<u>Sample size</u>	<u>Sample size</u>
Neutral	1.0034	1.0035	1.0041	1.00367
1% Acid	1.0044	1.0039	1.0046	1.00430
5% Acid	1.0042	1.0045	1.0048	1.00450
10% Acid	1.0042	1.0044	1.0049	1.00450
Average	1.0040 ₅	1.0040 ₇	1.0046 ₀	

Table 1b. High-Temperature Data
Acidity/Sample Size Experiment

Experimental $^{235}\text{U}/^{238}\text{U}$ Ratios for U500 Standard

	40 μg	200 μg	400 μg	Average
	<u>Sample size</u>	<u>Sample size</u>	<u>Sample size</u>	<u>Sample size</u>
Neutral	1.0008	1.0024	1.0027	1.00197
1% Acid	1.0006	1.0030	1.0028	1.00213
5% Acid	1.0008	1.0026	1.0026	1.00200
10% Acid	1.0012	1.0021	1.0035	1.00227
Average	1.0008 ₅	1.0025 ₂	1.0029 ₀	

The problems caused by gross variation in sample size, purity, or acidity are best controlled by good chemical preparation. Solutions must be essentially free of alkali elements, and in particular, potassium which is the source of complex ions that make significant background contributions at the 234 and 236 mass positions. Even with good chemistry it becomes essential to develop and observe rigid procedures for mounting the samples for analysis. The volume of solution per filament, the conversion of the nitrate to oxide, and positioning of the sample filaments with respect to the ionizing filament must be uniform and is, as far as possible, identical for each sample loading.

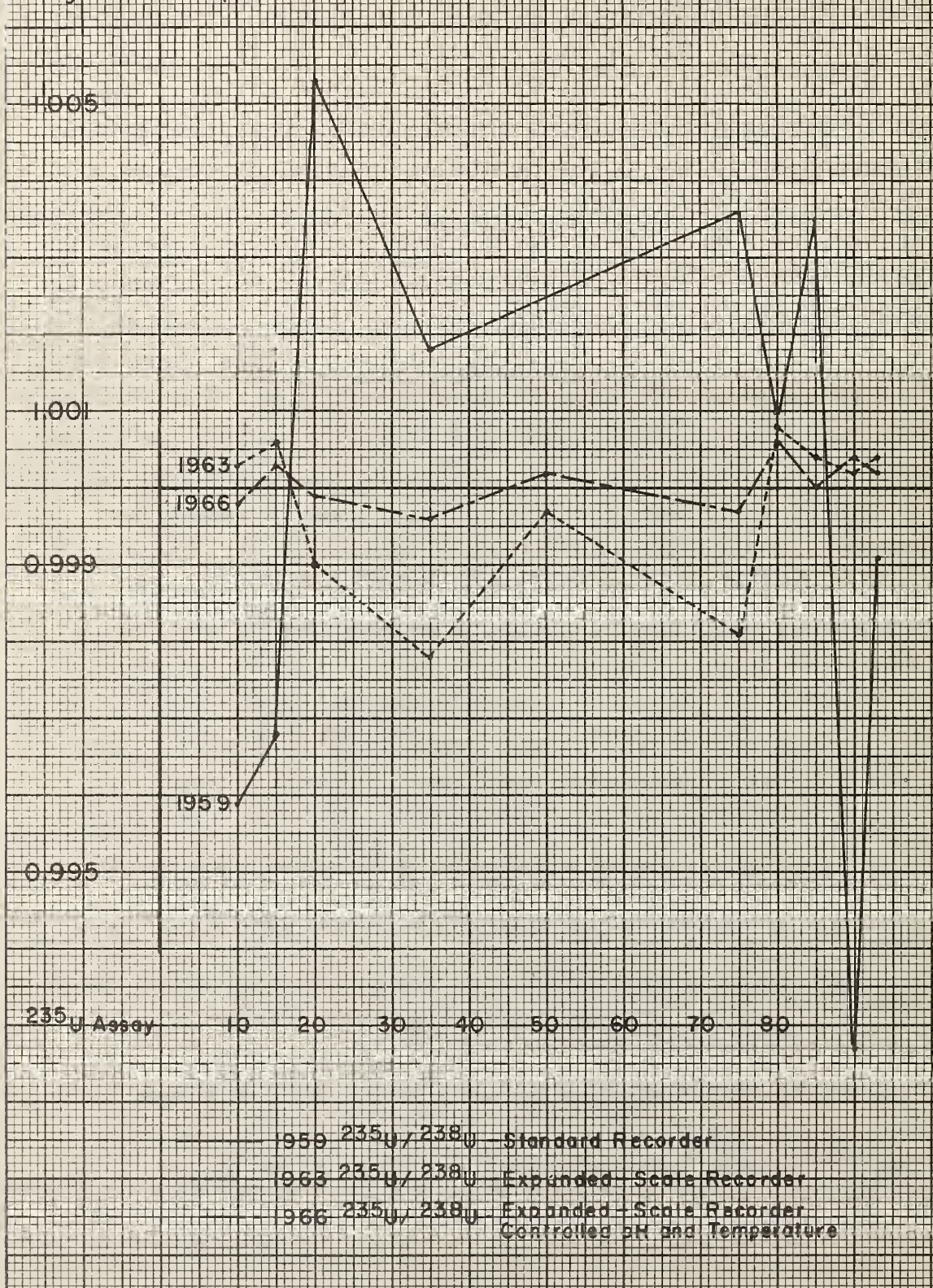
Efforts to control the temperature of the filaments are further complicated by variations in the dimensions of the rhenium ribbon. This dimensional variation is large enough to cause a difference of 1 A. in producing a 2150°C temperature. Sample filaments are operated at temperatures less than 1650°C and the current range due to dimensional variation is normally 0.3 A. Therefore, two filaments drawing identical currents are not necessarily at the same temperature, and it is dangerous to rely solely on current readings as an indication of temperature. If it is assumed that sample filaments at the same temperature will yield approximately equal signal intensities, a signal-current relationship can be established and is an effective means of controlling the temperature of the sample filaments. The signal-current relationship for low-temperature analysis is 3×10^{-11} A for a sample filament current range of 2.2 to 2.5 A and is based on the long term performance of many sample loadings. Significant deviation from this relationship is cause for rejection of the analysis.

Under the conditions described for low-temperature and high-temperature analyses the experimental $^{235}\text{U}/^{238}\text{U}$ ratios are always greater than the theoretical ratios. This bias is in the range of 0.50% for low-temperature and 0.25% for

high-temperature. The procedure for both of these techniques is identical during the first six minutes of heating when all effort is concentrated on obtaining a stable ^{187}Re signal of 6.5×10^{-12} A. During the remaining 24 minutes, until data are taken, the procedures differ in sample filament temperature and consequently, in signal intensities. This temperature differential is the prime factor in causing different fractionation rates which result in a characteristic average bias for each technique. Even after 2 hours of heating the biases of high-temperature and low-temperature analyses are still significantly different but are nearer zero-bias. This is especially true of high-temperature analyses where the bias is expected to decay to less than 0.15%. The bias of a low-temperature analysis after 2 hours of heating is normally greater than 0.3%. Once the ratio has decreased significantly for either technique the direction of change cannot be reversed by lowering the filament temperature. However, depending upon the combination of parameters selected, and with proper care the bias can be controlled at any given level over about a 1% range with better than 0.1% precision.

The ratio of the corrected experimental $^{235}\text{U}/^{238}\text{U}$ ratio to the "best estimate" of the theoretical $^{235}\text{U}/^{238}\text{U}$ is a dimensionless number and provides an effective means of comparing data taken at different times in the history of this laboratory. Three groups of data are presented in Figure 12 for comparison. The 1959 data were taken on a standard-recorder and each point on the graph is the average of 2 analyses corrected for zero bias. This group of data followed closely the first effort of this laboratory to measure uranium isotopic abundances and the graph is typical of standard-recorder data before 1960. The 1963 data were taken on an expanded-scale recorder and each point is a single $^{235}\text{U}/^{238}\text{U}$ analysis corrected for 0.13% bias. Both the 1959 and 1963 data were measured under high-temperature

Figure 12 Experimental $^{235}\text{U}/^{238}\text{U}$ vs Theoretical $^{235}\text{U}/^{238}\text{U}$



conditions but neither is characterized by control of acidity or the rigid analytical procedures of later measurements.

The interval between the first expanded-scale measurements of 1963 and the 1966 expanded-scale data was a period of identifying bias components and developing procedures to control them. All aspects of an analysis - chemistry, mounting procedures, and the mass spectrometer procedure - were rigidly controlled for the 1966 measurements. A single low-temperature analysis was made for each standard and the experimental $^{235}\text{U}/^{238}\text{U}$ ratios were corrected for 0.46% bias. The 95% limit of error per determination for the 1959, 1963, and 1966 data are 0.96%, 0.24%, and 0.07%, respectively.

1. Interim Procedure for Boron

Chemistry

Weighted quantities of boric acid and Na_2CO_3 are mixed to yield a Na/B ratio of 1:1 and the solution is evaporated to dryness. The final solution is adjusted to a concentration of 1 mg of boron per ml.

Mass Spectrometry

A single-filament tantalum source is used. One drop of solution ($\sim 20 \mu\text{g}$ of boron) is placed on an ionizing filament and dried with an infrared heat lamp for 10 minutes.

Boron is measured as the $(\text{Na}_2\text{BO}_2)^+$ ion at an accelerating voltage of 10 kV. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the tube pressure is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

Time from start
(minutes)

Procedure

- | | |
|-----|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0-2 | The ionizing filament current is slowly increased until the boron signal is detectable on the grid. This will require a current of approximately 1.1 A. Locate mass 88 ($\text{Na}_2^{10}\text{B}^{16}\text{O}_2$) and focus for maximum signal intensity. Increase the filament current until the $(\text{Na}_2^{10}\text{B}^{16}\text{O}_2)^+$ signal is 25 mV (2.5×10^{-13} A). |
| 6 | Increase the filament current to give a 50 mV ($\text{Na}_2^{10}\text{B}^{16}\text{O}_2$) signal. |
| 15 | Data-taking begins. The $(\text{Na}_2^{10}\text{B}^{16}\text{O}_2)^+$ signal should be 20-30 mV and decaying. Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps. |

Notes

The boron signal is normally decaying during most of the analytical time. On the basis of a limited number of sample

loadings it appears that, if the $(\text{Na}_2^{10}\text{B}^{16}\text{O}_2)^+$ signal is adjusted to 5×10^{-13} A, the signal will decay to an intensity of approximately 3×10^{-13} A within 10 minutes. During the next 15 minutes the rate of decay is significantly less and a precise ratio determination can be made. $(\text{Na}_2^{10}\text{B}^{16}\text{O}_2)^+$ signal intensities in the 10^{-12} A range are obtainable but the rate of decay is excessive and the signal will often reach 1×10^{-13} A before the analysis is completed.

Under carefully controlled conditions the $^{10}\text{B}/^{11}\text{B}$ ratio does not change significantly (0.2%) during the data-taking period. The filament is operated between 1.1 and 1.3 A, and at this current range a very faint red glow can be detected in the filament. When the filament is operated significantly above 1.3 A or at red-heat, very large (10^{-11} A) ion currents are obtained, but are decaying rapidly. Under these conditions the ratio shows significant fractionation.

Boron samples of known Na/B ratio (1:1, 1:2, and 2:1) were used to evaluate the effect of sodium content on the $^{10}\text{B}/^{11}\text{B}$ ratio determination. All samples were analyzed using the same analytical procedure. The observed $^{10}\text{B}/^{11}\text{B}$ ratio for the solution with the 2:1 Na/B ratio was lower (1%) than the observed ratios for the other samples.

All filaments are pre-baked at 3 A for 1 hour in a vacuum and under a potential field. Baked filaments are free of background signals at the mass 88 and 89 positions when operated at 2 A. Tantalum was selected as the filament material because significant $(\text{Na}_2\text{BO}_2)^+$ ion currents were not formed off rhenium or tungsten. Preliminary investigations with platinum ribbon have since indicated that it is a more efficient ionizing surface for the $(\text{Na}_2\text{BO}_2)^+$ ion. Ion currents in the 10^{-11} A range were obtained without changing the sample size.

2. Interim Procedure for Lithium Chemistry

Lithium is dissolved in nitric acid and the final solution is adjusted so that the concentration is 100 μg Li/ml.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution ($\sim 2 \mu\text{g}$ Li) is placed on each sample filament and dried with a heat lamp for 10 minutes. The spacing between ionizing and sample filaments is increased by $1/32$ of an inch to eliminate sample evaporation by radiant heat.

The Li^+ signals are measured at an accelerating voltage of 5 kV. The source and collector slit openings are 5 and 40 mils, respectively. Analyses are begun when the tube pressure is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

Time from start
(minutes)

Procedure

- | | |
|-----|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 0-1 | The ionizing filament current is set to give a temperature of 1600°C (3.2 A), which is measured with an optical pyrometer. The sample filament currents are set at 0.1 A. The Li signal is very small and frequently not detectable. |
| 5 | The sample filament currents are increased until the ^7Li signal is 8 mV. The signal should begin to grow rapidly. |
| 15 | If the ^7Li signal is less than 500 mV, (5×10^{-12} A), the sample filament currents are increased until this intensity is achieved. The signal should double during the next 15 minutes and no further adjustments should be made. |

Data-taking begins. The ${}^7\text{Li}$ signal should be approximately 1 volt. Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

The observed ${}^6\text{Li}/{}^7\text{Li}$ ratio changes very rapidly with time and strict adherence to a rigid analytical procedure is essential. If for any reason the data cannot be taken between 30 and 40 minutes after the filaments are turned on, the analysis is rejected. The most common cause of rejection is excessive signal strength and/or excessive rate of signal growth.

Notes

Lithium is very sensitive to small changes in sample filament currents and there is constant danger of generating far more signal than is required for an analysis. Caution must be used in adjusting sample filament currents since 0.3 A is hot enough to yield growing ${}^7\text{Li}$ signals as large as 5×10^{-11} A. The Li signals grow strongly throughout the analysis and it is difficult to control or slow down the growth rate once the filaments approach thermal equilibrium. The smaller than usual (5 mils) source slit opening reduces the signal intensity which helps balance the growth rate but does not completely solve the problem. No extensive study of Li has been made at this laboratory, only occasional service analysis.

3. Interim Procedure for Rubidium

Chemistry

Mass spectrometric experimentation showed that the presence of other alkali elements in the rubidium samples does not generally interfere with the rubidium isotope analysis and no attempt is made to obtain pure rubidium in the usual chemical procedure.

Rubidium-bearing silicate minerals are decomposed in platinum dishes, with a mixture of hydrofluoric and sulfuric acids. After evaporation, the excess sulfuric acid is fumed off and the residue is ignited for 1 to 2 minutes over a Meeker burner. The ignited residue is digested with water and filtered. This procedure eliminates most cations; only magnesium accompanies the alkali metals in significant amounts in the filtrate. However magnesium has a deleterious effect on the rubidium analyses and, if it is present in the sample, a supplementary chemical procedure must be employed for its removal. Final solutions are adjusted to contain 10 μg of Rb per milliliter in the form of Rb_2SO_4 in neutral solution.

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution ($\sim 0.2 \mu\text{g}$ Rb) is placed on each sample filament and dried with a heat lamp and a 0.25 A current for 5 minutes. The Rb_2SO_4 deposit is colorless and not detectable with the naked eye, but a slight stain, due to impurities, is noticeable in most mineral samples. The ionizing filament is set 1/32 of an inch lower than normal in the source block. This reduces vaporization of the sample by radiant heat from the ionizing filament but does not appreciably decrease the ionization efficiency.

The Rb^+ signals are measured at an accelerating voltage of 3800 volts. This relatively low voltage is used to reduce the number of secondary electrons released by the reflected

ions. The source and collector slit openings are 7 and 40 mils, respectively. Analyses are begun when the tube pressure is $< 4 \times 10^{-7}$ torr.

The following analytical procedure is used:

<u>Time from start</u> <u>(minutes)</u>	<u>Procedure</u>
0-1	The ionizing filament current is set to give a temperature of 1600°C (~ 3.2 A), measured with an optical pyrometer. The sample filament currents are set at 0.25 A. The Rb signal is not normally detectable.
5	The sample filament currents are increased in increments of 0.1 A until the Rb ion current is detectable on the grid. The signal is focused for maximum intensity and the sample filament currents are adjusted to give a 0.5 volt ^{85}Rb signal. The signal should grow steadily.
15	The sample filament currents are adjusted to give a ^{85}Rb signal of 1 volt.
25	Data-taking begins. The ^{85}Rb signal should have grown to approximately 1.4 volts (1.4×10^{-11} A). Ten peak sets are taken over the next 10-12 minutes. Each peak is monitored for 1/2 minute and magnet changes are made in discrete steps.

Rubidium signals are easy to control and stabilize, but sensitive to small changes in filament current. 1/10 A too much current is sufficient to cause overheating and excessive signal. All analyses should be made on constant or slowly growing signals. Under these conditions the observed ratio does not change over the 12 minute period required for taking data.

Notes

The presence of magnesium has a very deleterious effect on the rubidium isotope analyses. The magnesium apparently suppresses the rubidium ionization and sample filament temperatures must be made abnormally high in order to obtain the standard signal intensity. Under these conditions the observed ratio always changes rapidly with time. All such analyses should be discarded and the sample should be reprocessed for the specific removal of the magnesium.

The standard Rb ion signal intensity is obtained with sample filament currents of 0.4 to 0.8 A. If these currents are increased to > 1 A, ionization of rubidium will occur on the surfaces of the sample filaments and the mixing of these ions with the normal thermally-formed ions will produce a bias effect. For this reason, any analysis which requires sample filament currents > 0.8 A is rejected.

The ionizing filaments are pre-baked at 5 A for 1/2 hour in a vacuum and under a potential field. Unbaked filaments produce a small background signal, but this becomes barely detectable after baking. Clean source assemblies give no background signals but after a source has been used for 10 to 12 analyses a background Rb signal becomes detectable and increases in magnitude with each additional analysis. To eliminate this background, without having to remove and clean the source, a copper, silver, or uranium (a number of elements will do) sample is analysed after each 10 to 12 rubidium analyses. These analyses reduce the rubidium background signal by baking out or coating over the rubidium deposits on the source.

If a sample solution contains an excess of H_2SO_4 it will not dry properly on the filament. Attempts to force drying by increasing the temperature will result in partial evaporation of the rubidium and cause discrepancies in the mass spectrometric measurements. It is therefore essential that all sample solutions be neutral.

4. Interim Procedure for Strontium

Mass Spectrometry

A triple-filament rhenium-ribbon source is used. One drop of solution ($5\text{ }\mu\text{g Sr as SrCl}_2$) is placed on each sample filament and dried with a heat lamp and an electrical current which is increased until the filament has a faint red glow. The electrical current is adjusted in the following manner: 1.2 A for 5 minutes; 1.5 A for 1 minute; faint red glow (2.0 - 2.5 A) for 2 minutes.

The following analytical procedure is used:

<u>Time from start</u> <u>(minutes)</u>	<u>Procedure</u>
0	The ionizing filament current is set at 4.8 A. The sample filament currents are raised to give a 10 mV Sr grid signal ($\sim 0.5\text{ A}$).
2-3	The ionizing filament current is reduced to 3.8 A, (the signal decays). The sample filament currents are increased to give a 100 mV grid signal. The signal should be growing and no further changes are necessary.
15	Baseline readings are taken.
20	Data-taking begins. The grid signal should be $\sim 200\text{ mV}$ and should continue to grow slowly, or level off, for the remainder of the analysis.

With a slowly growing or stable signal, the observed ratios will not change over the data-taking period (20-25 minutes). If the signal should start to decay the run should be rejected; decaying signals generally show a significant change in observed ratio with time.

No extensive study of Sr has been made at this laboratory. The procedure given above was developed by Carl Hedge, of the U.S. Geological Survey.

C. APPENDIX

STATISTICAL EVALUATION OF UNCERTAINTIES ASSOCIATED WITH THE REPORTED VALUES

The determination of isotopic abundance ratios and atomic weights of selected elements by mass spectrometric methods as described above affords a good opportunity to illustrate how statistical methodology can be employed to advantage in the treatment of precision data. In the following, the general principles will be discussed first, followed by a detailed analysis for the determination of the atomic weight of bromine. Some of the additional problems that arise when there are more than two isotopes involved, e.g., chromium, are also briefly discussed.

The basic procedure used here, the same as in any other well-conceived calibration process, is to compare measurements on an unknown quantity with measurements on a known standard of similar magnitude by the same measurement process, and to derive the magnitude of the unknown from that of the standard. In performing an experiment of this type, the experimenter may wish to follow certain statistical principles and practices so as to strengthen the validity of his results. The essential ones that are used in this laboratory are discussed and illustrated below.

1. THE SEQUENCES AND NUMBERS OF MEASUREMENTS ARE CHOSEN SO AS TO INSURE THAT THE UNCERTAINTY DUE TO RANDOM ERRORS CAN BE REALISTICALLY ESTIMATED.

It is a practice in this laboratory to make the analyses of the unknown and standards in an alternate pattern, by different operators and instruments, and over periods of weeks or months. In between times, "runs" on other elements are routinely performed and the instruments taken apart for cleaning and adjustments. The results should show agreement within the indicated uncertainties unless the precision was over-estimated or there exist systematic errors which have not been accounted for.

2. BOUNDS TO SYSTEMATIC ERRORS ARE INVESTIGATED EXPERIMENTALLY AND REPORTED.

All measured isotopic ratios for a particular determination are corrected by the same "calibration factor" which is determined by measuring isotopic ratios of synthetic mixes of separated isotopes having "known" ratios. The uncertainties in the fractions of the isotopes in the separated isotopes, and in the chemical procedure devised to make the synthetic mixes, persist to the end as systematic errors in the calibration factor for the particular determination. The bounds to these errors are ascertained, generally from data obtained through multiple analysis of standards, and reported separately from the precision of the mass spectrometric ratio determination.

Other sources of possible systematic errors are also investigated. Known sources related to systematic errors of comparatively large magnitudes are traced and eliminated, if possible, in the preliminary investigation.

3. THE ASSUMPTIONS UNDERLYING THE STATISTICAL ANALYSIS ARE EXPERIMENTALLY VERIFIED IF POSSIBLE.

(a) In the statistical analysis the measured isotopic ratios and functions of these ratios are frequently used. For instance, the fraction f_1 of ^{107}Ag in a separated sample " $\text{Ag } 107$ " is calculated from the observed ratio r_1 of $^{107}\text{Ag}/^{109}\text{Ag}$ by the formula

$$f_1 = \frac{r_1}{1 + r_1} ,$$

and the standard deviation of f_1 is computed by the approximate formula

$$\text{s.d. of } f_1 \approx \frac{\text{s.d. of } r_1}{(1 + r_1)^2} .$$

A confidence interval for f_1 is then computed by the use of a Student's "t" statistic.

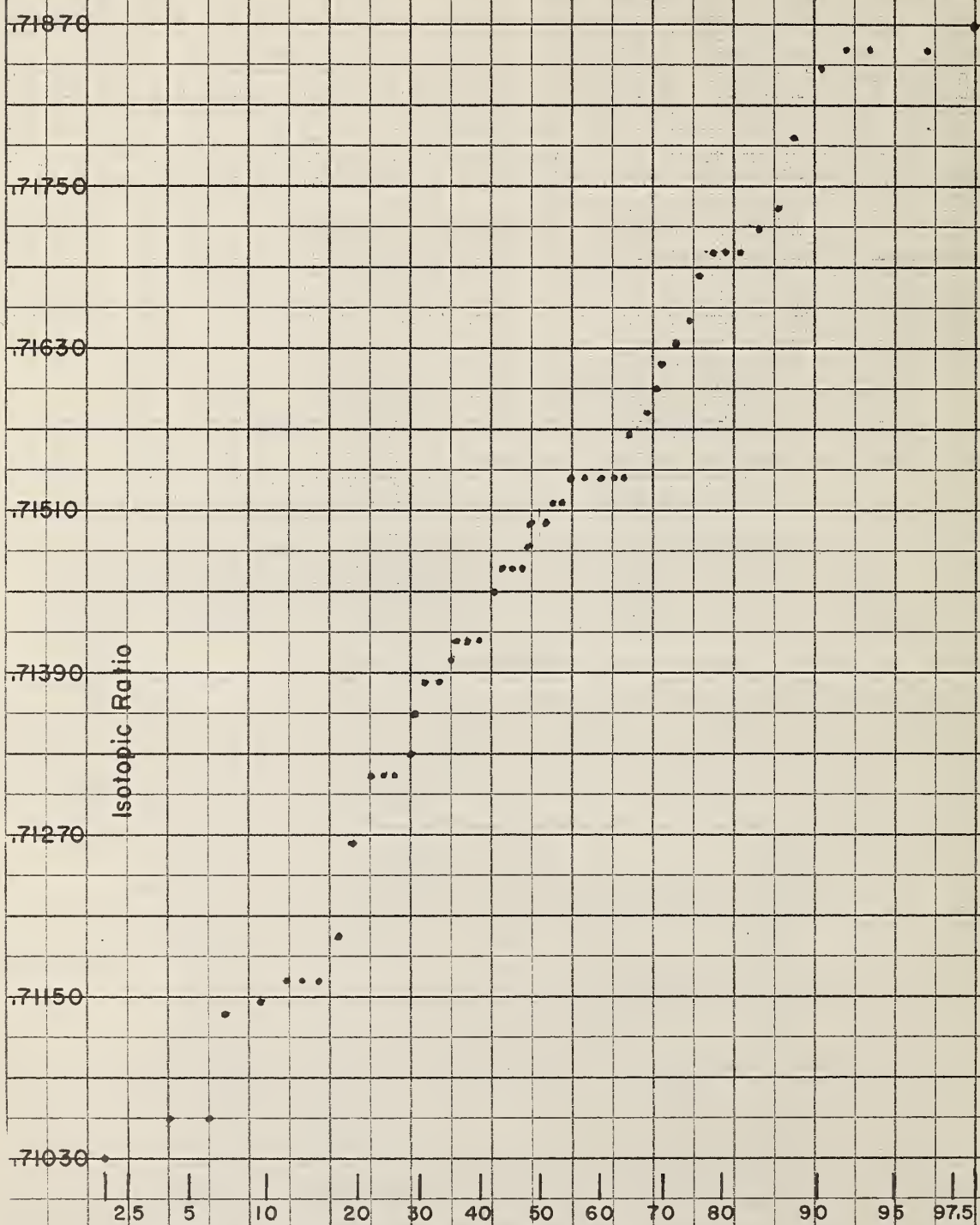
The justification of the use of this type of formula for the standard deviation of a ratio and for the use of confidence intervals based on Student's "t" statistic rests on a theorem

given by E. C. Fieller (see, for example, Handbook of Physics, Condon and Odishaw, p. 1-150). This theorem shows that such a ratio will be approximately normal with approximate standard deviation given by the classical propagation of error formula, if the variables are normally distributed, and if the ratio of average to standard deviation of the variable in the denominator is greater than 5. For all measured isotopic ratios the ratio of the average to standard deviation is greater than 100. The near linearity of 53 measurements of magnesium $^{24}/^{25}$ ratios plotted on normal probability paper in figure 1, gives evidence in support of the assumption of approximate normality. In the bromine example given below, the individual values are really averages of 9 determinations which in itself is usually sufficient to achieve approximate normality.

(b) From the observed ratios of the separated isotopes, the isotopic ratios of the synthetic mixes can be calculated. The comparison of observed to the computed ratios of the synthetic mixes yields the first calibration factor for the instrument. The observed ratios of the separated isotopes are then corrected by this calibration factor and the process repeated again to give a second calibration factor, etc. Although we have not proved mathematically that the results of the iteration process necessarily converge to a constant, in practice two to three iterations usually give the required accuracy. The five steps of the iteration for the calibration factor for silver were as follows:

	<u>Calibration Factor</u>	
first round (assumed)	1.0	
Δ_1	(.00532	96695)
second round	.99467	03305
Δ_2	(.00022	37934)
third round	.99444	65371
Δ_3	(.00000	94272)
fourth round	.99443	71099
Δ_4	(.00000	03976)
fifth round	.99443	67123

Figure 1 Normal Probability Plot of Observed Isotopic Ratios $^{24}/^{26}$ of Magnesium Reference Sample

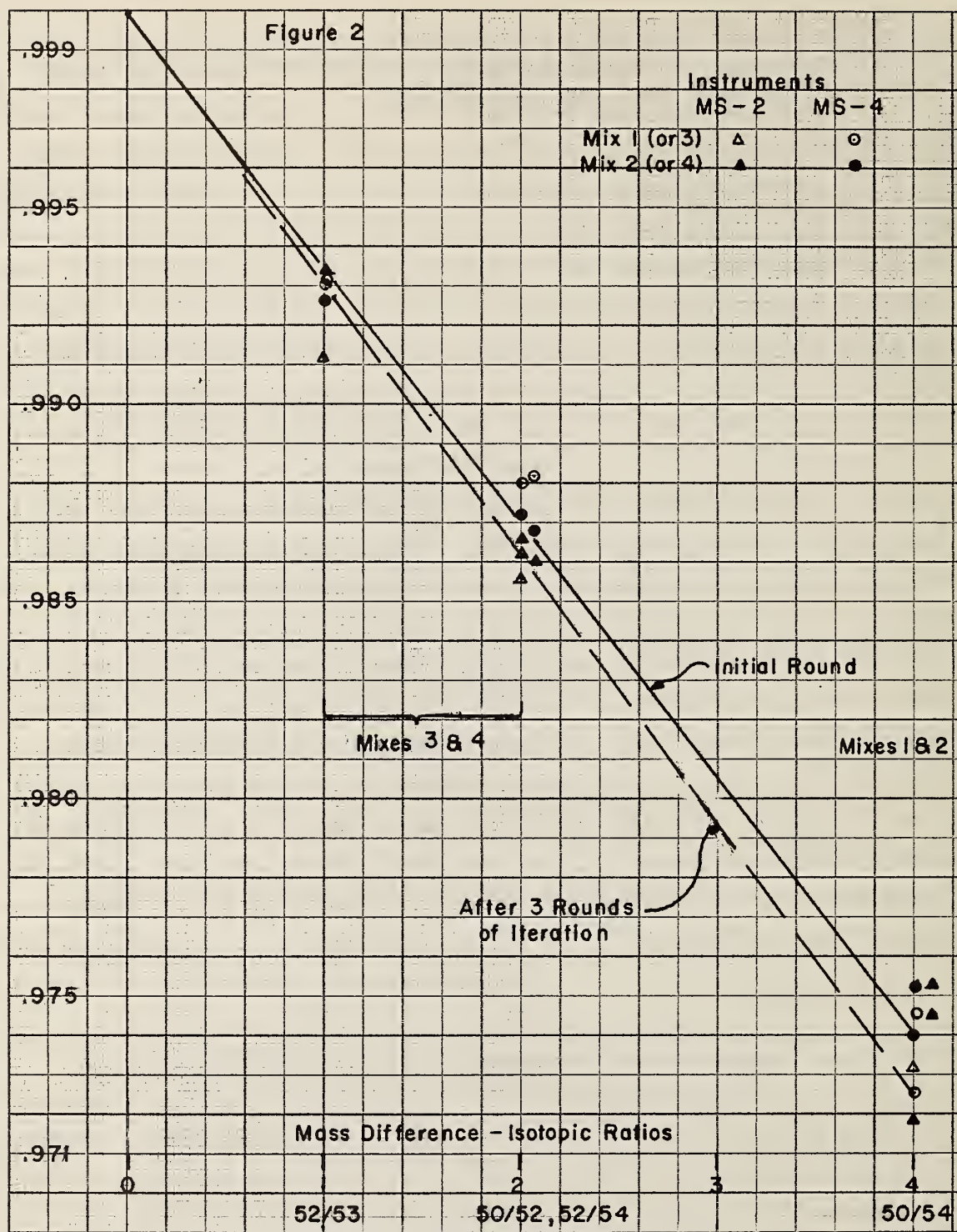


(c) In the case of chromium, four isotopes 50, 52, 53, and 54 are involved. The calibration factors, k_1 for 50/52, k_2 for 53/52, and k_3 for 54/52, were all computed from the calibration factor k for 50/54 using Mix I and Mix II. This was done on the theoretical ground that if measurement errors were the same, the calibration factor for 50/54 would have the maximum relative precision. The values of k_1 , k_2 , and k_3 thus obtained were checked against values obtained directly from an independent auxiliary experiment using Mix III and Mix IV. The result, shown in figure 2, lends support to the assumption that the calibration factors for ratios are linearly related to the mass differences of the isotopes.

(d) In computing the final uncertainties, all the known systematic errors and the random errors are propagated through the sequence of calculations involving ratios and functions of ratios. If the numerator and denominator are functionally or statistically related, the propagation of error formulas usually shown for independent variables no longer apply. For functionally related variables, it is easiest to express all the variables in terms of a single variable. Take chromium again as an example. Let f_{52} be the atom percent of isotope 52 in the reference sample, a , b , c be the observed ratios of 50/52, 53/52, and 54/52, with calibration factors k_1 , k_2 , and k_3 respectively, then

$$f_{52} = \frac{1}{1 + k_1 a + k_2 b + k_3 c} = \frac{1}{1 + k_1 a + \frac{2b}{1 + k_1} + \frac{c}{k_1}} .$$

$$= \frac{k_1^2 + k_1}{k_1^3 a + k_1^2 (a + 1) + k_1 (1 + 2b + c) + c} = \frac{N}{D} .$$



Comparison of observed calibration factors for isotopic ratios 52/53, 50/52, and 52/54 of Chromium with values computed from the observed calibration factor for the 50/54, assuming a linear relationship between the calibration factor and the mass difference of the isotopes.

Thus, the systematic error in f_{52} due to the error in determination of k_1 is

$$\Delta f_{52} \approx \frac{\Delta k_1}{D^2} \{ D(2k_1 + 1) - N[3ak_1^2 + 2(a+1)k_1 + (1 + 2b + c)] \}.$$

For variables that are statistically related the problem is much more complicated, since a reliable estimate of the degree of correlation is usually not obtainable from the available data. The experimenter must therefore strive to obtain measurements that are not correlated, through proper scheduling of his measurements and through careful consideration of the physical factors involved. A plot of one variable against the other, e.g., isotopic ratios r_1 against r_2 , would usually bring out any significant correlation between the variables. Other simple statistical tests may also be used. In our analysis these tests showed lack of significant correlation.

In addition, the use of propagation of error formulas does not take into account sources of error that are not included in their formulation, e.g., the possible differences between instruments and operators. These two sources of error, believed to be the most important, were investigated by performing independent experiments, using different instrument-operator combinations. The results were compared against their assigned uncertainties to check the validity of the assumed formulation. Such comparisons were made for the experiments on copper, bromine, and chromium, and found to be satisfactory.

The complete analysis for the determination of the atomic weight of bromine (in the form of the original memo, with minor modifications for clarification) is given below as an illustration of the various steps involved in arriving at the reported uncertainties. The summary page gives the values and the total and component uncertainties reported in Tables 5 and 8 in "Absolute Isotopic Abundance Ratio and the Atomic Weight of Bromine" by Catanzaro et al., J. Research NBS 68A, No. 6, 1964.

Memorandum

TO : Mr. W. R. Shields, 15.06

DATE: January 28, 1964

FROM : H. H. Ku, 11.03

SUBJECT: Determination of Atomic Weight of Bromine

Results on the analysis of data from you and Mr. T. Murphy for the isotopic ratio and atomic weight of bromine are summarized in the table below. The detailed calculations are given in the succeeding pages.

SUMMARY TABLE

<u>Isotopic Ratio</u>		
	<u>Det. I</u>	<u>Det. II</u>
Machine 4	1.028090	1.027803
Machine 1	1.027807	1.027669
<u>Average isotopic ratio</u>	$^{79}\text{Br}/^{81}\text{Br}$:	1.02784 \pm .00105
Uncertainty components:		
(95% confidence limits on ratio det.		\pm .00051)
(Possible error in composition of separated samples [isotopic]		\pm .00033)
(Possible error in synthetic mixes [chemical]		\pm .00021)
<u>Composition of Reference Sample</u>	^{79}Br : 50.686%	\pm .025
	^{81}Br : 49.314%	\pm .025
Uncertainty components:		
(95% confidence limits on ratio det.		\pm .0123)
(Composition of separated samples [isotopic]		\pm .0080)
(Synthetic mixes [chemical]		\pm .0051)
<u>Atomic Weight of Bromine:</u>		79.90363 \pm .00051
Uncertainty components:		
(95% confidence limits on ratio det.		\pm .00025)
(Composition of separated samples [isotopic]		\pm .00016)
(Composition of synthetic mixes [chemical]		\pm .00010)

A. Isotopic Compositions of the Two Separated Isotope Samples
"Br 79" and "Br 81".

Seven runs were made on separated sample "Br 79" (on instrument No. 4) and six runs on "Br 81" (on instrument No. 1), yielding ratios r as listed in Table 1. The correction factors used, .998364 (instrument No. 4) and .999513 (instrument No. 1), were based on results of measurements on synthetic samples in determination I and II after two iterations. No further iteration was found to be necessary.

The averages and computed standard deviations for \bar{r} and f are as follows:

Separated Sample	n	\bar{r}	s.d. of \bar{r}	f (Fraction of ^{79}Br)	s.d. of f	Half width of 95% C.I. on f
"Br 79"	7	378.480	1.895	.9973648	.0000132	.0000323
"Br 81"	6	258.108	1.822	.0038594	.0000271	.0000697

The maximum uncertainty (Δf) in the fraction determinations was taken to be .00008. Systematic error was assumed to be negligible.

B. Synthetic Samples and Analytic Error in Concentration Determinations.

The concentrations of the "Br 79" and "Br 81" solutions for the two determinations were as follows:

	<u>Det. I</u>	<u>Det. II</u>
"Br 79" solution	.340394	.361610
"Br 81" solution	.327176	.352875

The standard deviation of the analytic method for an analysis was computed to be .00004736 meg/g, based on 17 analyses of the separated isotope solutions and 17 analyses of three solutions of Normal NaBr. The detailed data are given in Tables IIa, b, and c. The standard error of the concentrations (average of four analyses used) of separated bromine solutions was computed to be .00002368 with 27 degrees of freedom.

Table 1

Analysis of Separated Samples

"Br 79"			"Br 81"		
Run No.	r(79/81)	r(corr.)	Run No.	r(81/79)	r(corr.)
4-2601	378.49	377.87	1-1902	260.30	260.43
-2602	386.73	386.10	-1903	253.62	253.74
-2603	372.41	371.80	-1904	253.87	253.99
-2604	379.84	379.22	-1905	262.33	262.46
-2605	383.57	382.94	-1906	254.56	254.68
-2606	377.34	376.72	-1907	263.22	263.35
-2607	375.32	374.71			

$$\begin{aligned}\bar{r} &= 378.480 \\ f &= .9973648\end{aligned}$$

$$\begin{aligned}\bar{r} &= 258.108 \\ f &= .0038594\end{aligned}$$

$$\begin{array}{lll} s^2(r) & 25.1349 & 19.9198 \\ s^2(\bar{r}) & 3.5907 & 3.3200 \\ s_{\bar{r}} & 1.895 & 1.822 \end{array}$$

$$s_f = \frac{1.895}{(379.48)^2} = .0000132$$

$$\frac{1.822}{(259.108)^2} = .0000271$$

$$\begin{aligned} t_{(6,.05)} s_{\bar{r}} &= 2.447 \times .0000132 & 2.571 \times .0000271 &= .0000697 \\ &= .0000323 \end{aligned}$$

Table 2a

Analysis of Concentration of Separated Sample Solutions

DETERMINATION I

"Br 79"				"Br 81"			
Sol.	Wt. of sol.	meq.	C meq./g.	Sol.	Wt. of sol.	meq.	C meq./g.
A	7.53019	2.56406	.340 504	A	9.09645	2.97587	.327 146
B	8.21278	2.79583	.340 424	B	8.65398	2.83156	.327 197
C	8.54475	2.90845	.340 379	C	8.07874	2.64328	.327 190
D	8.26555	2.81273	.340 296	D	7.81712	2.55753	.327 170
E	7.77453	2.64618	.340 365				

$$\begin{aligned}\bar{C} &= .340\ 394 \\ s^2(C) &= .0000\ 0000\ 5917\ 3 \\ S(C) &= .0000\ 7692\end{aligned}$$

$$\begin{aligned}\bar{C} &= .327\ 176 \\ s^2 &= .0000\ 0000\ 0524\ 25 \\ S &= .0000\ 2290\end{aligned}$$

DETERMINATION II

"Br 79"				"Br 81"			
Sol.	Wt. of sol.	meq.	C meq./g.	Sol.	Wt. of sol.	meq.	C meq./g.
A	7.77112	2.810027	.361 599	A	7.78525	2.74700	.352 847
B	7.88535	2.851350	.361 601	C	7.58655	2.67682	.352 838
C	7.32444	2.648832	.361 643	D	7.09924	2.50502	.352 857
D	7.73096	2.795487	.361 596	E	7.47154	2.63715	.352 959

$$\begin{aligned}\bar{C} &= .361\ 610 \\ s^2 &= .0000\ 0000\ 0495\ 58 \\ S &= .0000\ 2226\end{aligned}$$

$$\begin{aligned}\bar{C} &= .352\ 875 \\ s^2 &= .0000\ 0000\ 3177\ 58 \\ S &= .0000\ 5637\end{aligned}$$

Table 2b

Analysis of Concentrations of Normal NaBr, Meq/g

	3A	5	6B
	.336 280	.288 819	.303 309
	.336 275	.288 865	.303 149
	.336 289	.288 789	.303 254
	.336 321	.288 811	.303 181
	.336 296	.288 884	.303 197
	.336 295		.303 191
	<hr/>	<hr/>	<hr/>
\bar{c}	.336292667	.2888336	.3032135

$s^2(c)$.0000 0000 0261 1	.0000 0000 1559 8	.0000 0000 3351 1
$s(c)$.0000 1616	.0000 3949	.0000 5789

Table 2c

Estimated Precision of Chemical Analysis

Analysis of Normal NaBr

<u>Sample</u>	<u>n</u>	<u>Degrees of freedom</u>	<u>s^2</u>	<u>$(n-1)s^2$</u>
3A	6	5	.0 ⁹ 261066	.0000 0000 13053
5	5	4	.0 ⁸ 15598	.0000 0000 62392
6B	6	5	.0 ⁸ 33511	.0000 0001 67555

Analysis of Separated SamplesDet. I

"Br 79"	5	4	.0 ⁸ 59173	.0000 0002 36692
"Br 81"	4	3	.0 ⁹ 52425	.0000 0000 15728

Det. II

"Br 79"	4	3	.0 ⁹ 49558	.0000 0000 14868
"Br 81"	4	3	.0 ⁸ 31776	.0000 0000 95328
<hr/>				
Total		27		.0000 0006 05616

Combining the above	s_p^2	=	.0000 0000 22430
	s_p	=	.0000 4736

$$\text{For averages of 4 det.: } s_{\bar{c}} = \frac{s_p}{\sqrt{4}} = .00002368$$

$$\text{For averages of 5 det.: } s_{\bar{c}} = \frac{s_p}{\sqrt{5}} = .00002118$$

Table 2d

Analysis of Normal NaBr

Set	No.	Weight Solution g	Bromide Calculated meq	Bromide Found meq	Assay %
3A	1	8.27566	2.78461	2.78294	99.940
	2	7.51737	2.52946	2.52790	99.938
	3	8.05733	2.71115	2.70959	99.943
	4	7.82072	2.63153	2.63027	99.952
	5	8.21018	2.76258	2.76105	99.945
	6	8.27691	2.78504	2.78348	<u>99.944</u>
Average					99.944
5	1	7.32550	2.11707	2.11574	99.937
	3	8.28530	2.39446	2.39333	99.953
	4	8.89337	2.57019	2.56831	99.927
	5	9.55065	2.76014	2.75833	99.934
	6	10.71678	3.09716	3.09391	<u>99.960</u>
Average					99.942
6B	1	8.16336	2.47695	2.47602	99.962
	2	7.56806	2.29632	2.29425	99.910
	3	10.18410	3.09008	3.08837	99.945
	4	8.65015	2.62465	2.62256	99.920
	5	9.62452	2.92029	2.91813	99.926
	6	9.13134	2.77065	2.76854	<u>99.924</u>
Average					99.931

The ratio of the bromide meq found by this method of analysis to that of bromide meq calculated for the three normal NaBr solutions averaged to better than 99.93% as shown in Table 2d.

Five synthetic mixes were used in determination I and six in determination II. These mixes were prepared from about equal weighted amounts of solutions "Br 79" and "Br 81". Let

$$G = (W_{81}/W_{79}) (\text{meq } 81/\text{meq } 79),$$

then $\Delta G \approx (W_{81}/W_{79}) \Delta(\text{meq } \frac{81}{79}),$

the weighing error in W being negligible. Taking $(\text{meq } \frac{81}{79})$ to be the half-width of the 95% confidence interval on meq $\frac{81}{79}$,

$$\Delta(\text{meq } \frac{81}{79}) \approx 2.052 \times \frac{\text{meq } 81}{\text{meq } 79} \left[\frac{1}{(\text{meq } 81)^2} + \frac{1}{(\text{meq } 79)^2} \right]^{1/2} \times .00002368.$$

The value of ΔG for both determinations was taken to be .0002 (see Table 6).

The computed isotopic ratio μ for a synthetic mix is

$$\mu = \frac{1 + G}{f_1 + f_2 G} - 1$$

where

$$f_1 = .0026352 = \text{fraction of } 81 \text{ in "Br 79"}$$

$$f_2 = .9961406 = \text{fraction of } 81 \text{ in "Br 81"}.$$

$$\text{Then } \Delta \mu \approx \frac{(1 + G)^2}{(f_1 + f_2 G)^2} \Delta f + \frac{f_2 - f_1}{(f_1 + f_2 G)^2} \Delta G.$$

The values of μ are listed in Table 3. The value of $\Delta \mu$ was calculated to be .000536 with components as follows:

$$.000328 \quad \text{due to } \Delta f \quad (.00008)$$

$$.000208 \quad \text{due to } \Delta G \quad (.0002) \quad .$$

Table 3

Composition of Synthetic Mixes

DETERMINATION I

Mix No.	W_{79}	W_{81}	W_{81}/W_{79}	$\frac{meq}{(81/79)}$	G
1	2.20305	2.23035	1.0123919	.9611689	.9730796
3	2.03553	2.08166	1.0226624	"	.9829513
4	2.07995	2.11262	1.0157071	"	.9762661
5	2.11338	2.11904	1.0026782	"	.9637431
6	2.17520	2.24607	1.0325809	"	.9924846
	$\frac{1+G}{-}$	$\frac{f_2 G}{-}$	$\frac{f_1 + f_2 G}{-}$	$\frac{1+G}{f_1 + f_2 G}$	$\frac{\mu}{-}$
	1.9730796	.9693241	.9719593	2.030002	1.03000
	1.9829513	.9791577	.9817929	2.019725	1.01972
	1.9762661	.9724983	.9751335	2.026662	1.02666
	1.9637431	.9600236	.9626588	2.039916	1.03992
	1.9924846	.9886542	.9912894	2.009993	1.00999

DETERMINATION II

Mix No.	W_{79}	W_{81}	W_{81}/W_{79}	$\frac{meq}{(81/79)}$	G
1	1.04618	1.08450	1.0366285	.975844	1.0115877
2	1.09963	1.09671	.9973446	"	.9732527
3	1.09990	1.10046	1.0005091	"	.9763408
4	1.09030	1.09721	1.0063377	"	.9820286
5	1.18382	1.07291	1.9063118	"	.8844189
6	1.10534	1.20550	1.0906147	"	1.0642693
	$\frac{1+G}{-}$	$\frac{f_2 G}{-}$	$\frac{f_1 + f_2 G}{-}$	$\frac{1+G}{f_1 + f_2 G}$	$\frac{\mu}{-}$
	2.0115877	1.0076836	1.0103188	1.991043	.99104
	1.9732527	.9694965	.9721317	2.029820	1.02982
	1.9763408	.9725727	.9752079	2.026584	1.02658
	1.9820286	.9782386	.9808738	2.020676	1.02068
	1.8844189	.8810056	.8836408	2.132562	1.13256
	2.0642698	1.0601624	1.0627976	1.942298	.94230

The error in μ due to bias in assay is negligible (approximately .000002) for solutions of ^{81}Br and ^{79}Br of about the same concentration.

C. Errors in the Correction Factors.

Duplicate determinations of ratios were carried out for each synthetic mix for the two instruments. The standard deviation of a determination was estimated from the differences of these duplicates (Table 4a and 4b).

Let C denote the correction factor and

$$\bar{C} = \frac{1}{n} \sum_{i=1}^n \frac{\mu_i}{x_i} ,$$

then since the value of C is near 1,

$$\sigma_{\bar{C}} \approx \frac{1}{\sqrt{n}} \cdot \frac{1}{\bar{\mu}} \sigma_x .$$

and

$$\Delta \bar{C} \approx \bar{C} \frac{\Delta \mu}{\bar{\mu}} .$$

Values of $\Delta \bar{C}$ and $\hat{\sigma}_{\bar{C}}$ are listed in Table 6.

D. Isotopic Ratios of Reference Sample.

In Table 5, the observed isotopic ratios of the reference sample Y are listed for the two determinations and the two machines. Computations were carried out for

$$\bar{Y}^* = \bar{C} \bar{Y} ,$$

$$\Delta \bar{Y}^* \approx \bar{Y} (\Delta \bar{C}), \text{ and}$$

$$\sigma_{\bar{Y}} \approx \sqrt{\bar{C}^2 (\sigma_{\bar{Y}})^2 + \bar{Y}^2 (\sigma_{\bar{C}})^2} ,$$

are listed in Table 6. Since the range of the four values of \bar{Y}^* was well within the estimated uncertainty of an individual value, the four values were averaged, yielding an isotopic

Table 4a

Analysis of Synthetic Mixes

DETERMINATION I

Syn. Mixes	INST. 4			INST. 1		
	X	μ	$C_4 = \frac{\mu}{X}$	X	$C_1 = \frac{\mu}{X}$	
1	1.0306			1.0303		
	<u>1.0301</u>			<u>1.0291</u>		
	1.03035	1.03000	.999670	1.0297	1.000301	
3	1.0213			1.0202		
	<u>1.0211</u>			<u>1.0209</u>		
	1.0212	1.01972	.998561	1.02055	.999197	
4	1.0286			1.0282		
	<u>1.0287</u>			<u>1.0282</u>		
	1.02865	1.02666	.998075	1.0282	.998512	
5	1.0408			1.0412		
	<u>1.0417</u>			<u>1.0409</u>		
	1.04125	1.03992	.998723	1.04105	.998915	
6	1.0120			1.0115		
	<u>1.0127</u>			<u>1.0120</u>		
	1.01235	1.00999	.997679	1.01175	.998270	
	Average	1.02526	.9985416		.9990390	

$$\sum (\text{diff. bet. dup.})^2 = 387 \times 10^{-8}$$

$$S_X^2 = \frac{1}{2 \times 10} \times 387 \times 10^{-8} = .0000001935$$

$$S_X = .00044$$

$$\sigma_C^{\wedge} = \frac{.00044}{1.025 \sqrt{10}} = .000136$$

Table 4b

Analysis of Synthetic Mixes

DETERMINATION II

Syn. Mixes	INST. 4			INST. 1		
	X	μ	$C_4 = \frac{\mu}{X}$	X	$C_1 = \frac{\mu}{X}$	
1	<u>.99341</u> <u>.99196</u> .992685			<u>.9909</u> <u>.9914</u> .99115		.999899
2	<u>1.0330</u> <u>1.0315</u> 1.03225			<u>1.0293</u> <u>1.0299</u> 1.0296		1.000214
3	<u>1.0295</u> <u>1.0280</u> 1.02875			<u>1.0271</u> <u>1.0276</u> 1.02735		.999260
4	<u>1.0222</u> <u>1.0232</u> 1.0227			<u>1.0207</u> <u>1.0218</u> 1.02125		.999442
5	<u>1.1341</u> <u>1.1344</u> 1.13425			<u>1.1311</u> <u>1.1326</u> 1.13185		1.000627
6	<u>.94323</u> <u>.94386</u> .943545			<u>.9422</u> <u>.9415</u> .94185		1.000478
Average		<u>1.02383</u>	<u>.9981858</u>			<u>.9999866</u>

$$\sum (\text{diff. bet. dup.})^2 = 1289.94 \times 10^{-8}$$

$$S_X^2 = \frac{1}{2 \times 12} \times 1289.94 \times 10^{-8} = .00000054$$

$$S_X = .000735$$

$$\frac{\Delta}{\sigma_C} = \frac{.000735}{1.024 \sqrt{12}} = .000210$$

ratio of $\bar{Y}^* = 1.02784$ for this experiment. Table 6 lists the values, systematic errors, and standard errors, for results of determinations I and II.

E. Composition of Reference Sample.

The isotopic composition P of the reference sample is given by

$$P = \frac{\bar{Y}^*}{1 + \bar{Y}^*} = \frac{1.02784}{2.02784} = .506864$$

$$\begin{aligned} \Delta P &\approx \frac{1}{(1 + \bar{Y}^*)^2} (\Delta \bar{Y}^*) = \left(\frac{1}{2.02784}\right)^2 (.00033 + .00021) \\ &= (.000080 + .000051) \end{aligned}$$

where the first component is due to Δf and the second due to ΔG .

$$\hat{\sigma}_P \approx \left(\frac{1}{2.02784}\right)^2 (.000252) = .000061.$$

The half width of a 95% C.I. on P = $2.020 \times .000061 = .000123$.

F. Atomic Weight of Reference Sample.

$$W = N_{81} - (N_{81} - N_{79})P = 79.90363$$

based on

$$\begin{aligned} N_{81} &= 80.916344 \\ N_{79} &= 78.918348 . \end{aligned}$$

$$\Delta W \approx 2.00 \quad \Delta P = (.00016 + .00010)$$

$$\hat{\sigma}_W \approx 2.00 \quad \hat{\sigma}_P = .000122$$

$$\begin{aligned} \text{Half width of 95\% C.I. on } W &= 2.020 \times .000122 \\ &= .00025 . \end{aligned}$$

Table 5

Y = Ratios 79/81 for Reference Sample

DETERMINATION I		DETERMINATION II	
Instrument No. 4	Instrument No. 1	Instrument No. 4	Instrument No. 1
1.0292	1.0289	1.0296	1.0284
294	285	293	270
298	287	302	279
302	294	305	269
294	290	288	273
296	286	294	261
293	291	299	286
295	293	290	286
300	288	296	283
297	298	299	283
296	274	299	268
294	280	300	280
Ave. 1.029592	1.028792	1.029675	1.027683
s_Y^2 .000000086	.00000041	.00000024	.00000069
s_Y .00029	.00064	.00049	.00083
$s_{\bar{Y}}$.00008	.00018	.00014	.00024

Table 6 Comparison of Determinations I and II

Values	DETERMINATION I		DETERMINATION II	
	S.E. (d.f.)	(n)	(n)	S.E. (d.f.)
meq 79	.0 ⁴ 2118(27)	.340394(5)	.361610(4)	.0 ⁴ 2368(27)
meq 81	.0 ⁴ 2368(27)	.327176(4)	.352875(4)	.0 ⁴ 2368(27)
meq 81 79	.0 ⁴ 916	.961169	.975844	.0 ⁴ 915
$\Delta \text{meq } \frac{81}{79} = 1/2(95\% \text{C.I.})$.0001878	.0001878	
$\Delta G = \frac{\bar{w}_{81}}{\bar{w}_{79}} \Delta \text{meq}$.0001910	.0001887	
Take ΔG equal to		.0002	.0002	
$f_1 = 81/"\text{Br } 79"$.0 ⁴ 132(6)	{.0026352 {.9961406	Same as DET. I	
$f_2 = 81/"\text{Br } 81"$.0 ⁴ 271(5)		ditto	
Take Δf equal to		.00008	ditto	
$\Delta \mu$.000536 { .000328 .000208	ditto	
$\bar{c}_4 (\bar{c}_4 = .998364)$.0 ³ 136(10)	.9985416	.9981858	.0 ³ 210(12)
$\bar{c}_1 (\bar{c}_1 = .999513)$.0 ³ 136(10)	.9990390	.9999866	.0 ³ 210(12)
$\Delta \bar{c}_4 \text{ or } \Delta \bar{c}_1$.00052 { .000320 .000200	Same as DET. I	
\bar{y}_4	.0 ⁴ 84(11)	1.029592	1.029675	.0 ³ 14(11)
\bar{y}_1	.0 ³ 19(11)	1.028792	1.027683	.0 ³ 24(11)

$$\begin{aligned} \bar{Y}_4^* &= \bar{C}_4 \bar{Y}_4 \\ \bar{Y}_1^* &= \bar{C}_1 \bar{Y}_1 \\ \Delta \bar{Y}^* & \end{aligned}$$

$$\begin{aligned} .0^3 163 & \quad 1.028090 & \quad 1.027803 & \quad .0^3 258 \\ .0^3 236 & \quad 1.027807 & \quad 1.027669 & \quad .0^3 323 \end{aligned}$$

$$.000535 \left\{ \begin{array}{l} .000329 \\ .000206 \end{array} \right. \quad \text{Same as DET. I}$$

Final Reported Isotopic Ratio

$$\begin{aligned} \bar{Y}^* &= 1.02784 \\ \Delta \bar{Y}^* &= .000535 \left\{ \begin{array}{l} .000329 \text{ due to } \Delta f \\ .000206 \text{ due to } \Delta G \end{array} \right. \\ \sigma \bar{Y}^* &= .000252 \quad \text{with 44 d.f.} \end{aligned}$$

Total uncertainty on Ratio (= 1.02784)

$$\begin{aligned} \text{Due to separated samples} & \quad .00033 \\ \text{Due to synthetic mixes} & \quad .00021 \\ \text{Half-width of 95\% C.I.} & \\ = 2.020 \times .000252 & \quad .00051 \\ \hline \text{Total uncertainty} & \quad .00105 \end{aligned}$$



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